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Identification and Listing of Hazardous Waste Under RCRA (Resource Conservation and Recovery Act), Subtitle C, Section 3001; Listing of Hazardous Waste; Finalization of July 16, 1980 Hazardous Waste List (40 CFR 261.31 and 261.32)

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This document is one of a series providing support for regulations issued by the U.S. Environmental Protection Agency (EPA) under Subtitle C of the Resource Conservation and Recovery Act (RCRA). The regulations represent the initial effort for nationwide control of hazardous waste from point of generation, through transportation, treatment, and storage, to point of ultimate disposal.

This document covers listing of hazardous wastes from specific and nonspecfic sources. The solid wastes of concern in this document are muds from brine purification, and wastewater treatment sludges from the mercury cell process in chlorine production. The constituent of concern in these wastes is the toxic heavy metal mercury.

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BACKGROUND DOCUMENT

IDENTIFICATION AND LISTING OF HAZARDOUS WASTE
UNDER RCRA, SUBTITLE C, SECTION 3001

Listing of Hazardous Waste; Finalization of July 16, 1980, Hazardous Waste List (40 CFR 261.31 and 261.32)

This document (ms. 1941.28a) provides background information
and support for EPA's hazardous waste regulations

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LISTING BACKGROUND DOCUMENT

CHLORINE PRODUCTION

K071: BRINE PURIFICATION MUDS FROM THE MERCURY CELL PROCESS IN CHLORINE PRODUCTION WHERE SEPARATELY PREPURIFIED BRINE IS NOT USED (T).

K106: WASTEWATER TREATMENT SLUDGE FROM THE MERCURY CELL PROCESS IN CHLORINE PRODUCTION (T).

I. SUMMARY OF BASIS FOR LISTING

The solid wastes of concern in this document are muds from brine purification, and wastewater treatment sludges from the mercury cell process in chlorine production. The constituent of concern in these wastes is the toxic heavy metal mercury.

The Administrator has determined that mercury-bearing sludges and muds resulting from the mercury cell process in chlorine production are solid wastes which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and which therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. These wastes are generated in large quantities and contain significant concentrations of mercury. At the present time approximately 39,500 kkg of hazardous mercury-bearing wastes are generated each year. These wastes are calculated to contain about 154 kkg of mercury. Large quantities of this highly toxic pollutant are thus available for environmental release.

2. These wastes have been involved in a number of serious damage incidents, demonstrating empirically that improper waste management may result in substantial environmental hazard.

II. SOURCES OF THE MERCURY AND TYPICAL DISPOSAL PRACTICES

A. Industry Profile

Twenty-seven facilities, located in 16 states, are engaged in chlorine and either sodium hydroxide or potassium hydroxide manufacture using the mercury cell process.(1,2,24) These facilities are identified in Tables 1 and 2. In 1980, their mercury cell production capacity was reported as ranging from 27,000 to 232,000 kkg per year.(24)

B. Manufacturing Process(1,3,22,24)

In the mercury cell process, rock or evaporated salt is dissolved in recycled brine or in fresh water in agitated tanks to form a saturated salt brine. In plants not using prepurified salt--most of the plants using this process--[*] this brine is purified by adding soda ash and sodium hydroxide, and in some cases barium salts, precipitating barium sulfate, calcium carbonate and magnesium hydroxide. These filtered muds (A in Figure 1) are removed by settling and filtration, and constitute one of the wastes of concern. The purified brine is then fed to the electrolytic mercury cells, where it is decomposed by electrolysis to produce chlorine and

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[*] Eight presently operating facilities (listed in Table 2) use evaporated rock salt already purified in on-site diaphragm cell operations; these plants do not perform significant purification, and therefore do not generate mercury-containing brine muds.

TABLE 1

FACILITIES PRODUCING MERCURY-BEARING BRINE PREPARATION/PURIFICATION MUDS.(24)

STATE	FACILITY	ROCK SALT SOURCE	CHLORINE CAPACITY 10^3 kkg/yr	HAZARDOUS BRINE MUDS TOTAL, DRY BASIS (kkg/year)
AL	Diamond Shamrock, Mobile	IA	38	981
	Diamond Shamrock, Mus.Sho.	IA[1]	132	2124
	Stauffer Chemical, LeMoyne	IA	70	1400
DL	Diamond Shamrock, Del.City	NY[1]	132	4750
GA	Olin Corporation, Augusta	IA	100	1818
IL	Monsanto Co., Sauget	IA[1]	40	600
KY	Convent Ch'l, Calvert City	IA	116	2914[3]
	Pennwalt Corp., Calvert City	IA	114	3147[3]
IA	Stauffer Chem., St.Gabriel	IA	170	2500
ME	Intl.Minerals, Orrington	NY	72	900
NJ	Linden Chemicals, Linden	NY	145	2900
NY	Hooker Sobin, Niag. Falls	Sask.KCl[2]	45	703[3]
	Olin Corp., Niag. Falls	NY	84	2325
NC	Linden Products, Acme	IA	54	540
OH	International Minerals, Ashtabula	Sask. KCl	33	800[3]
TN	Olin Corp., Charleston	TN	230	4230
WA	Georgia Pacific, Bellingham	Prepurif. evap.	76	336[3]
WI	Vulcan Materials, Pt.Edwards	MI	66	3360
			1717	36,328

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1. Also use KCl for KOH production.
2. New York Rock salt also used prior to 1972.
3. Brine muds combined with all other mercury-containing wastes.

~~4~~

Table 2

FACILITIES WHICH DO NOT PRODUCE MERCURY-BEARING BRINE MUDS.(24)

STATE	FACILITY	MERCURY CELL CHLORINE CAPACITY 10^3 kkg/yr	SALT SOURCE
AL	Olin Corp., McIntosh	132	Solution mined.
GA	Linden Chemicals, Brunswick	92	Solar purified, evaporated, dissolved in recycle brine.
LA	BASF Wyandotte Corp., Geismar[b]	-	-
LA	PPG, Lake Charles[a]	232	Louisiana
NC	Linden Chemicals, Acme	46	European evap. salt, pre-purified.
NY	Linden Chemicals, Syracuse[d]	27	New York State
TX	Diamond Shamrock, Deer Park[a]	99	Texas
TX	Alcoa, Point Comfort[d]	150	Texas brine, pre-purified, evap., diss. in recycle brine.
WV	PPG, Natrium	60	West Virginia
WV	Linden Chemicals, Moundsville	76	Solution-mined, evap., diss. in recycle brine
		914	

(a) These facilities use pure salt obtained from on-site diaphragm cell operations; no hazardous brine preparation muds are generated.

(b) Facility closed in 1979.

(c) Prior to 1970 brine purification operations were conducted in the mercury cell circuits, therefore some of the accumulated wastes from this site may be hazardous.

(d) Prior to 1970 rock salt was used, and mercury-containing brine muds were generated.

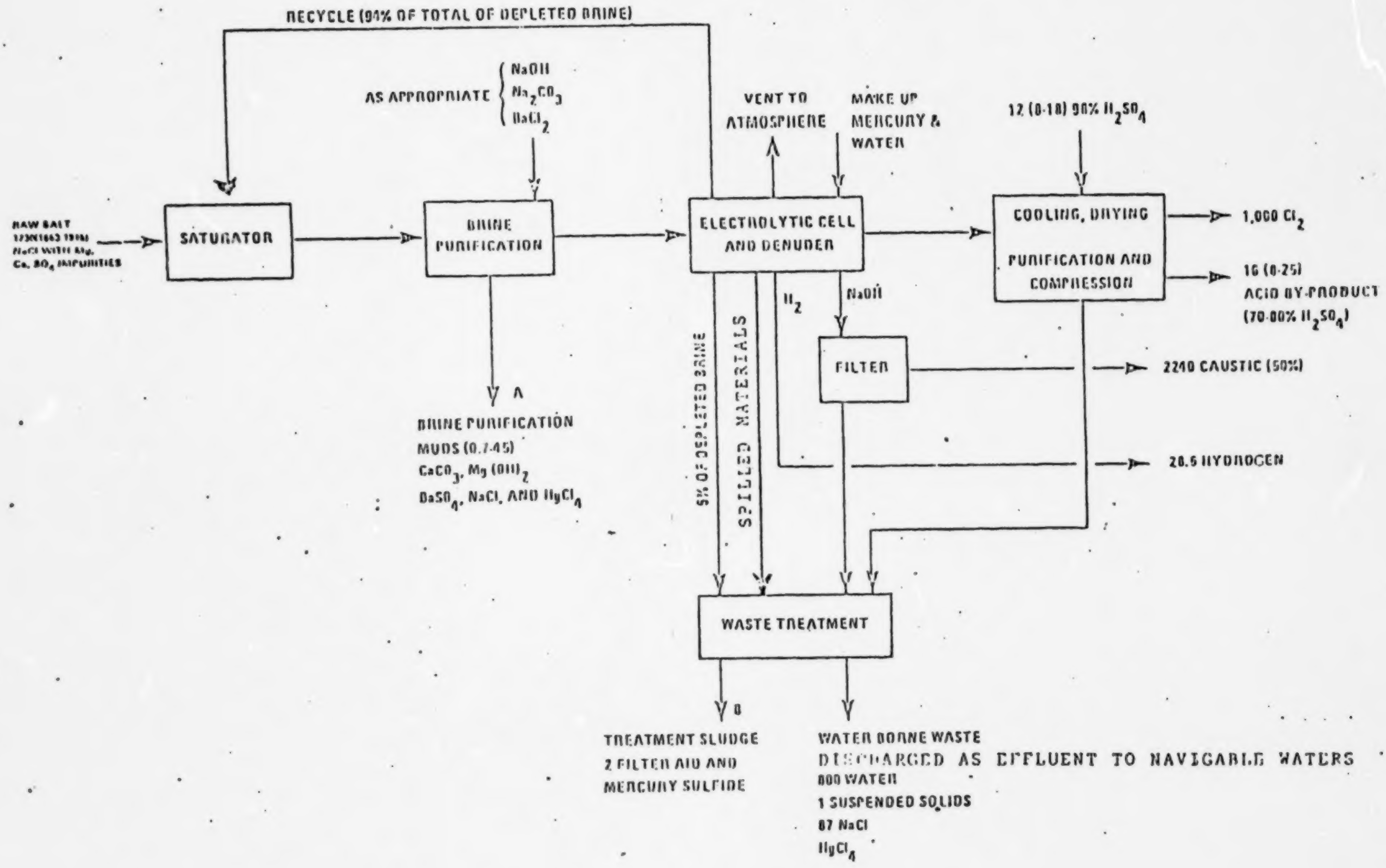
RECYCLE (94% OF TOTAL OF DEPLETED BRINE)
RAW SALT
NaCl WITH Mg,
Ca, SO_4 IMPURITIES
SATURATOR
AS APPROPRIATE
NaOH
Na_2CO_3
$BaCl_2$
BRINE PURIFICATION
A
BRINE PURIFICATION
MUDS (0.7-45)
$CaCO_3$, $Mg(OH)_2$
$BaSO_4$, NaCl, AND $HgCl_4$
VENT TO ATMOSPHERE
MAKE UP MERCURY & WATER
ELECTROLYTIC CELL AND DENUDER
H_2
NaOH
FILTER
5% OF DEPLETED BRINE
SPILLED MATERIALS
12 (8-18) 98% H_2SO_4
COOLING, DRYING
PURIFICATION AND COMPRESSION
1,000 Cl_2
16 (8-25)
ACID BY-PRODUCT
(70-80% H_2SO_4)
2240 CAUSTIC (50%)
28.5 HYDROGEN
WASTE TREATMENT
B
TREATMENT SLUDGE
2 FILTER AID AND
MERCURY SULFIDE
WATER BORNE WASTE
DISCHARGED AS EFFLUENT TO NAVIGABLE WATERS
800 WATER
1 SUSPENDED SOLIDS
87 NaCl
$HgCl_4$

FIGURE 1 CHLOR-ALKALI MANUFACTURING BY MERCURY (1)

sodium amalgam. The spent brine from the mercury cells is dechlorinated and approximately 94% is returned (recycled) to the initial brine make-up for resaturation; the remainder is discharged to wastewater treatment.

Since some of the feed of the brine purifier is a mercury-bearing recycle stream from the electrolytic cell, the muds (A in Figure 1) resulting from brine purification are contaminated with mercury. According to data provided by the Chlorine Institute, muds contain from 13-1000 ppm, averaging about 200 ppm of mercury.(24)

In all plants, the depleted purged brines from the electrolytic cell, together with two other waste streams generated from ancillary processes, are channeled to waste treatment. Wastewater treatment generates sludges (B in Figure 1) in amounts averaging 1.4 kg of sludge per kkg of chlorine product.(24) These wastes, contain about 0.2 to 15% of mercury, with an average concentration of 4.2% mercury(24), and constitute the second waste of concern.

The mercury leaving the cells in the form of sodium mercury amalgam is sent to denuders where the amalgam is decomposed at 80°C by the addition of deionized water. Water reacts with the sodium mercury amalgam to produce a 50 percent solution of sodium hydroxide* essentially free of sodium chloride. This solution is filtered to recover entrained mercury. The waste from the filtration step is sent to wastewater treatment, where mercury precipitates into the treatment sludge (stream B). Entrained mercury is removed from the hydrogen generated in the denuders, and returned to the electrolytic process. After removal of mercury, the hydrogen is either compressed for sale, used on-site, or used as a fuel. The chlorine gas collected in the electrolytic cells is cooled to condense out excess water vapor. This stream, which is essentially free of mercury, is sent to waste treatment. The partially dried chlorine is then scrubbed with 98 percent sulfuric acid to remove the rest of the entrained water vapor and is collected, compressed and liquified.

C. Waste Generation

The wastes of interest in this document are muds that result from the treatment of rock salt and recycled depleted brine, and sludges generated by the treatment of purged, depleted brines and ancillary waste streams. Seventeen facilities (see Table 1) generate both of these wastes. Eight other operating facilities, (those which use prepurified or evaporated salt - see Table 2) do not generate brine purification muds (waste A, Figure 1).(24)

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*Potassium hydroxide is produced in plants using potassium chloride as raw material.

The source of mercury in the brine purification muds is the recycled brine from the electrolytic cell (which mercury is removed in the purification process step).

These brine preparation muds contain substantial concentrations of mercury, in elemental form, and as oxides, chlorides and the complex ion, $HgCl_4^{=}$. Earlier data indicated that the concentration of mercury in these muds ranges from 500(12) to 2000 ppm(13,14). More recent data, however, indicate that the concentration of mercury in these muds ranges between 13-1000 ppm, with an average concentration of 200 ppm in samples from fifteen facilities.(24) Even at the new reported levels, the total potential mercury loadings are substantial: using the 1980 figure (ref. 24) the 36,000 kkg of hazardous brine preparation and purification muds generated each year (Table 1) are therefore estimated to contain 7 kkg of mercury.

It should be noted that the amount of muds produced depends on the source of the salt used as raw material.(11,12) Facilities using salt from the Texas-Louisiana salt dome generate about 10 kg of brine mud per kkg of chlorine. Plants using other salt sources generate brine muds in amounts ranging from about 20 kg per kkg of chlorine (salt from Kansas and New York) to 45 kg per kkg chlorine (salt from Michigan and West Virginia deposits). All the above quoted figures are on a dry-weight basis.(1,10,11,12)

The sludges resulting from wastewater treatment consist mainly of mercuric sulfide. Approximately 3,500 kkg of this waste is generated annually.(24) It contains mercury in concentrations ranging from 0.02 to 15%, with an average concentration of 4.2%.(24) Therefore 147 kkg of mercury are generated in the wastewater treatment sludges each year.

In total, therefore, of the approximately 39,500 kkg of hazardous mercury-bearing wastes from the mercury cell process for the production of chlorine, approximately 154 kkg of mercury are generated annually from the mercury cell process for the production of chlorine. A 1965 study(15) estimated that 846 kkg of mercury were lost to the environment from this industry as both water borne and solid wastes, and air emissions.

D. Waste Management (1,11,12)

Of the seventeen plants generating both listed waste streams, all but five combine their wastes prior to treatment. One plant retorts all mercury-containing wastes, eight others retort only the mercury-rich wastes, and of these eight, four store these wastes in drums until decisions are made on final disposal. One plant sends sludges to contractors for recovery. This latter disposal method is occasionally used by other facilities. Nine plants now use on-site pond storage of sludges, and seven use on-site landfill. Four plants send wastes to contractors for secured landfilling. Several plants employ combinations of these treatment and disposal techniques.*/

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*/ One plant utilizes a relatively new system for recovery of mercury from virtually all mercury bearing wastes. Treatment of contaminated wastes with sodium hypochlorite leaves wastes with a residual mercury content of less than 8 ppm.(24) The treated waste is then disposed of by landfilling. This waste recovery process is in theory capable of treating brine mud and of recycling recovered mercuric chloride. However, its applicability is limited by cell design and water balance considerations.

II. DISCUSSION OF BASIS FOR LISTING

A. Hazards Posed by the Waste

The two listed wastes are of regulatory concern because of their contamination with the toxic metal mercury. Brine preparation and purification muds are reported to contain as much as 1000 ppm of mercury, and treatment sludges contain about 4.2% mercury.(24) Moreover, very large amounts of these wastes (39,500 kkg) are generated. Mercury is highly toxic to a wide variety of organisms, including man, and can accumulate in biological organisms in its various forms.

These wastes have been involved in a number of damage incidents, demonstrating empirically that improper management of these wastes may cause substantial harm. These damage incidents are described below.

- The Olin 102nd Street Landfill, Niagara Falls, Niagara County, New York.(4)

  From mid 1948 to September, 1970 Olin Chemical Corporation utilized a landfill for the disposal of chemical wastes from its Niagara Falls plant. These wastes include brine sludge from a mercury cell chlor-alkali plant plus other wastes such as chlorinated organics, lime wastes, HTH wastes, fly ash, black cake wastes (sodium chloride, sodium chlorite, sodium chlorate, carbon, calcium carbonate, calcium hydroxide), graphite from electrolytic cells and concrete cell bodies, together with a limited amount of research materials. This landfill is located in a suburban section of Niagara Falls, New York, contiguous to the northern shore of the Niagara River. When it was closed, the landfill was "secured" by covering the waste with a soil cover, establishing vegetation, and by constructing a dike along the Niagara River.

In 1978, a surface and groundwater sampling program was initiated at the landfill site by RECRA Research Inc. and WEHRAN Engineering Corporation(5) to provide both baseline water quality data and sufficient information to assess the impact of previous disposal operations at the site. The program included the analysis of waters from the various groundwater regimes encountered on-site, and of grab samples of surface waters from the Niagara River. In view of the fact that the EPA National Interim Primary Drinking Water Standard for mercury is 2 ug/l, pertinent results indicated serious mercury contamination:

1) On one of the two dates on which samples were taken, all mercury analyses for the six Niagara River surface grab samples (taken downstream from the furthest upriver point where the landfill borders the river) contravened the Drinking Water Standard in every case, with values ranging from 4.7 to 15 ug/l. On the second date, there was no significant

difference in concentrations up- and down stream from the landfill site. On this date, stormy conditions prevailed, and the river flow was much above normal.

2) Water samples were taken from the fourteen piezometers located in the saturated water zone in the landfill. Soluble mercury readings ranged from non-detectable values to 40 ug/l, with the bulk of the readings ranging from 3.9 ug/l to 11 ug/l. Out of 14 samples taken, 13 contravened the Drinking Water Standard.

3) Contiguous to the saturated water zone of the landfill is a semi-confined aquifer of alluvial deposits. Water samples were taken from piezometers located in the alluvial deposits aquifer. Soluble mercury readings ranged from non-detectable to 35 ug/l. These data are believed to indicate that leachate from the landfill has migrated to this zone.

- The Newco Solid Waste Management Facility Niagara Falls, New York (5,6)

At this disposal site, Olin is currently disposing of brine sludges emanating from its mercury chlor-alkali process. (This site has been used as a waste disposal area for over 80 years.) An evaluation was performed of the presence, movement, and quality of groundwater at this facility, and the data were incorporated in a Draft Environmental Impact Statement for the State of

New York.(5,6) Elevated levels of mercury (6.6 ug/l) have been found in the leachate of mercury-contaminated sludges that have been disposed of in the landfill.

- In another damage incident(16) (involving an inactive chlor-alkali facility not otherwise identified in the literature), leaching of mercury from the solid wastes from the facility caused elevated levels of mercury in downstream water, suspended matter, and bottom sediment. About 39 kg of mercury are lost to water from this unlined lagoon each year. Concentration of mercury in water and suspended matter immediately downstream from the plant site are about 20 times higher than immediately upstream. The silt-clay fraction of bottom sediment immediately downstream of the plant site contains up to 200 times as much mercury as similar sediments collected immediately upstream from this facility.(16)

- Contamination of Surface Water from an Alkali Processing Plant in Saltville, Virginia(21):

  In another damage incident involving the Olin Corporation, an alkali processing plant generating the wastes listed in this document (and other industrial waste) disposed of these wastes in a series of lagoons located on the North Fork of the Holston River in Saltville, Virginia. Although the site (presently owned by Olin) ceased operating in 1972, wastes continue to leach from the disposal lagoons. Mercury continues to enter the Holston River both from the site of the chlorine plant and from disposal lagoons used for disposal of chlorine production wastes. The grounds where the cell building once stood are estimated to contain some 220,000 lbs. of mercury. Cleanup costs are estimated at $32-$40 million.

The incidents described demonstrate that mercury will migrate from mercury-bearing wastes in harmful concentrations and can cause substantial environmental harm unless proper management is assured.

There are also other factors which warrant listing these wastes as hazardous. Transportation of these wastes to off-site disposal facilities, a management practice utilized by several manufacturers, increases the likelihood of mismanagement of these hazardous wastes, for example, due to improper handling during transport, or failure to reach the intended destination. A transport manifest system combined with designated standards for the management of these wastes will greatly reduce their availability to do harm to human beings and the environment.

The quantity of these wastes generated is an additional factor of concern. As indicated above, these wastes are generated in large quantities (39,500 kkg of waste per year, containing 154 kkg of mercury). Under improper disposal conditions large amounts of mercury are thus available for environmental release. The large quantities of this contaminant poses the danger of polluting large areas of ground and surface waters.

Contamination will also occur over long periods of time, since elemental mercury persists indefinitely. Since large amounts of pollutants are available for environmental loading, the attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutants available. All of these considerations increase the possibility of environmental exposure to the harmful constituent in the wastes.

B. Health and Ecological Effects

The various forms of mercury are interconvertible under most environmental conditions. They are toxic to a wide variety of organisms, including man,(9) and are known to accumulate in biological organisms.(9) In humans, mercurials have been associated with neurological disorders, sensory impairment and tremors. Prenatal exposure can result in impaired brain development and psychomotor disorders. Organic mercury compounds inhibit fertility, and are more toxic than inorganic forms; 0.1 ug mercury/l is toxic to freshwater crayfish.(17) Mercury is bioconcentrated 63,000-fold in fathead minnows foraging under laboratory conditions resembling those in the field.(18) EPA estimates 200 ug/day as the acceptable daily intake and, in 1973, recommended 2 ug/l as a drinking water standard (20).

A World Health Organization expert group recommended 1 ug/l as an international standard for drinking water.(20)

For total recoverable mercury, the EPA has established criteria to protect aquatic life as 0.00057 ug/l and 0.025 ug/l for freshwater and saltwater species, respectively(26). For the protection of human health from the toxic properties of mercury ingested through waster and contaminated aquatic organisms the ambient water criterion is 0.144 ug/l.(20) Additional information and specific references on the adverse effects of mercury on human health and the environment can be found in Appendix A.

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Response to Comments: Chlorine Production (Mercury Process) Waste.

1. Several commenters stated that the Agency's characterization of the industry and the quantity and quality of its wastes was inaccurate in several respects, and provided new data on siting, production capacity, source of raw materials and the mercury content of wastes of concern. The listing background document was modified to reflect this new information. Both the original and the new data were provided by the Chlorine Institute, thus, in both instances, the Agency relies in large part on the accuracy and timeliness of the trade association's figures.

2. several commenters indicated that brine muds and wastewater treatment sludges pose very different risks of environmental harm, and argued that these two wastes should be accordeddifferent regulatory treatment. In particular, it was argued that brine muds ordinarily contain lower concentrations of mercury, and should not be considered irremediably hazrdous. It also was suggested that any of these wastes which pass the extraction procedure test should automatically not be regulated under subtitle C.

   The Agency agrees that the mercury content of these two wastes differs. However, we believe that mercury concentrations and potential mass loadings from brine muds alone are typically high enough to warrant listing.

Brine purification muds contain sufficient concentrations (13 - 1000 ppm by industry figures) and volumes (7kkg annually) of mercury to result in substantial environmental harm if mismanaged. Even muds containing low concentrations of mercury would need to leach only one hundredth to one thousandth of their total mercury to exceed the interim primary drinking water level of 0.002 ppm.

By listing these wastes the Agency is not precluding possible site-specific delistings if individual wastes do not meet the criteria for listing. Thus, facilities that treat their brine purification muds to reduce mercury concentrations could conceivably be able to delist their wastes. EP leachate results are certainly relevant, although not determinative, in making a delisting determination (see 45 FR 33111 - 33112, May 19, 1980). We reiterate however, that we believe ample evidence exists that the brine muds are typically hazardous, and therefore intend to retain the listing for this waste stream.

3. Two commenters argued that the listing of mercury-bearing brine sludges as hazardous is contrary to the purposes of RCRA, because it discourages industry efforts to render these wastes less hazardous. We again disagree. As the commenter and the background document point out, these wastes can be treated to recover mercury and reduce the mercury content. We believe this listing strongly encourages such treatment.

Should the resulting residue in fact be non-hazardous, the delisting mechanism allows individual facilities an opportunity to avoid regulation. Further, even if the resulting sludges are still hazardous wastes, it it should be much easier to obtain final management permits, again providing economic and managerial incentives for generators to develop or make greater use of technologies which can render such wastes non-hazardous.

4. One commenter argued that no environmental hazard has been shown to be associated specifically with mercury-bearing brine purification muds. The commenter pointed out that many varieties of mercury-bearing wastes were deposited at the sites for which the Agency documented mismanagement incidents. The Agency agrees that the several damage incidents, documenting contamination of water with mercury from landfills in which solid wastes from chlorine production had been disposed does not specifically implicate any one of these residues as being the unique cause of such contamination. Nor does the Agency deem it necessary to make such unique identification. The damage incidents and the published data concerning leaching of soluble mercury in solid wastes from a

chlor-alkali plant reported in the listing background document illustrate that water contamination from such wastes in toto does occur. Further, it appears probable that listed chlor-alkali wastes were responsible for at least some of the damage caused in these incidents. If the commenter were able to document the fact that mercury-bearing brine purification muds, when uniquely disposed for periods similar to those illustrated in the damage incidents, did not cause water contamination, this could constitute proof that such wastes might indeed not be hazardous. In the absence of such proof, however, the Agency will continue to list mercury-bearing brine purification muds as hazardous.

5. One commenter stated that, although poorly managed mercury-bearing wastes can result in environmental damage, such damage has resulted from wastes which were improperly managed in the past. The commenter felt it unreasonable to assume that such poor management practices would continue in the future.

It is the Agency's position that the fact that a waste is properly managed by particular generators or classes of generators does not render the waste non-hazardous. RCRA requires that EPA determine whether a waste is hazardous if substantial hazard could result when wastes are improperly treated, stored, transported, disposed of, or otherwise managed. The potential of the waste to cause hazard is the key factor. This position is more fully explained at 45 FR 33113.

6. One commenter suggests that the EP toxicity test should be the sole criterion for determining whether these wastes are hazardous. While the Agency has determined that the EP is a valid and acceptable test for identifying wastes likely to leach toxic constituents into groundwater, it believes the EP to be a somewhat less precise instrument than the listing mechanism for determining hazard, inasmuch as the EP fails to take into account factors such as the concentration of toxicants in the waste, their chemical composition, and the quantitity of waste generated, all of which have a bearing on the hazardousness of the waste. This position and the grounds for its determination are more fully discussed at 45 FR 33111. Therefore, the listing mechanism also may be used to bring wastes within the hazardous waste management system. Listing appears particularly appropriate here, where the wastes contain high concentrations of very toxic constituent, and are reliably believed to have caused substantial damage in acutal waste management practice.

LISTING BACKGROUND DOCUMENT

K073: CHLORINATED HYDROCARBON WASTE FROM THE PURIFICATION STEP OF THE DIAPHRAGM CELL PROCESS USING GRAPHITE ANODES IN CHLORINE PRODUCTION (T)

I. SUMMARY OF BASIS FOR LISTING

Chlorinated hydrocarbons are generated during the production of chlorine in diaphragm cells with graphite anodes. Purification results in separation of the chlorinated hydrocarbon waste from the product. The Administrator has determined that this waste is a solid waste which may pose a substantial hazard to human health and the environment when improperly transported, treated, stored, disposed of or otherwise managed, and which therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. The waste contains significant concentrations of the toxic compounds chloroform, carbon tetrachloride, hexachloroethane, trichloroethane, tetrachloroethylene, dichloroethylene, and 1,1,2,2-tetrachloroethane. The Agency's Carcinogenic Assessment Group has found that chloroform, carbon tetrachloride, tetrachloroethylene and 1,1,2,2-tetrachloroethane exhibit substantial evidence of carcinogenicity.

2. Typical management practices include deep well injection and incineration. Landfilling has also been employed as a disposal method. If these practices are unregulated, hazardous substances could be released to the environment. Improper construction or operation of a deep well could cause leakage of the waste from the well into usable aquifers; inadequate incineration can result in the generation of highly toxic combustion products such as phosgene. Uncontrolled landfilling may result in migration of hazardous substances to air and ground and surface waters.

3. Most of these compounds have significant migratory potential and have proven mobile and persistent in actual damage incidents caused by improper waste management.

II. SOURCES OF WASTE AND TYPICAL DISPOSAL PRACTICES

A. Industry Profile

Chlorine is produced by electrolysis of brine. It is used in the pulp and paper industry, plastics, water treatment and manufacture of organic and inorganic chemicals. About 75 percent of all chlorine manufactured in the United States is produced by the diaphragm cell process.( ) Approximately 32 plants use diaphragm cells; of these, six plants that utilize graphite anodes generate chlorinated hydrocarbon contaminants.*(1) Locations and production capacities of the six are given in Table 1.(2)

B. Manufacturing Process(1,3)

Brine is first purified by precipitation of metals before being sent to the diaphragm cell. Separation of solids during purification generates waste brine muds; the Agency has no data at this time to indicate that the brine muds are hazardous. The purified brine is heated, brought to saturation by the addition of salt and acidified. The saturated salt solution is then electrolyzed in the diaphragm cell to form chlorine, hydrogen and sodium hydroxide. Chlorine is liberated at the anode, and hydrogen and sodium hydroxide are produced at the cathode. Reaction of chlorine with

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*Graphite anodes predominated in the past, but in recent years most plants have replaced them with metal anodes.

Table 1

FACILITIES GENERATING CHLORINATED HYDROCARBON BEARING WASTES(2)

PLANT/LOCATION	PRODUCTION CAPACITY 10^3 KKG/YR
ICI Americas Baton Rouge, LA	156
Dow Chemical Midland, Mich.	256
Vulcan Materials Denver City, Tex.	121
Champion Production	
Canton, N.C.	26
Pasedena, Tex	20
PPG Industries Barberton, Ohio	100

carbonaceous materials in the graphite anode results in the presence of chlorinated hydrocarbon contaminants in the chlorine product.

The hydrogen is purified and either sold, vented to the atmosphere or burned. The salt solution, which has been decomposed to approximately half its original concentration, is partially evaporated to increase the sodium hydroxide concentration. During evaporation, most of the sodium chloride precipitates from the solution and is recovered in salt separators. After filtration and washing, the salt is recycled to initial brine preparation.

Chlorine is recovered from the cell and cooled to remove water and other impurities. The condensates are discharged or recycled to the brine purifier. After cooling, the chlorine gas is scrubbed with acid to remove residual water vapor. The gas is then compressed and cooled to -30°C to -45°C. At these temperatures, the chlorine liquefies and is pumped to steel storage tanks. Some further purification is performed during the cooling and liquefaction process. The chlorinated hydrocarbon waste of concern is liquefied from the chlorine gas stream during purification. Figure 1 illustrates the process.

The Agency is also concerned that wastewaters from clean-out of the diaphragm cell and from caustic evaporation and salt recovery operations and sludges resulting from treatment of these wastewaters may also be hazardous because

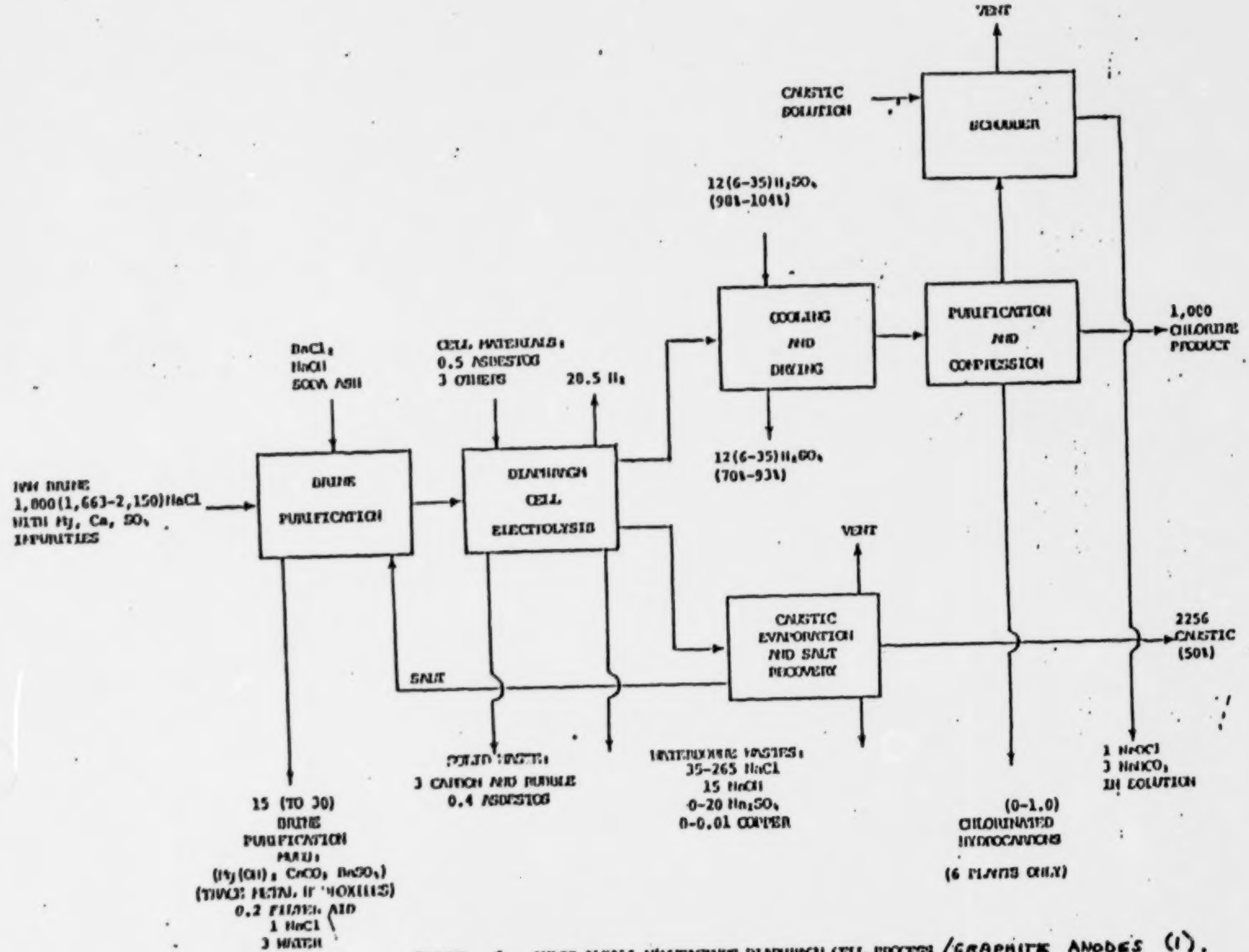
VENT
CAUSTIC SOLUTION
SCRUBBER
12(6-35)H₂SO₄ (90%-104%)
COOLING AND DRYING
PURIFICATION AND COMPRESSION
1,000 CHLORINE PRODUCT
BaCl₂ NaOH SODA ASH
CELL MATERIALS: 0.5 ASBESTOS 3 OTHERS
20.5 H₂
RAW BRINE 1,800(1,663-2,150)NaCl WITH Mg, Ca, SO₄ IMPURITIES
BRINE PURIFICATION
DIAPHRAGM CELL ELECTROLYSIS
12(6-35)H₂SO₄ (70%-93%)
VENT
CAUSTIC EVAPORATION AND SALT RECOVERY
2256 CAUSTIC (50%)
SALT
SOLID WASTE: 3 CARBON AND RUBBLE 0.4 ASBESTOS
WATERBORNE WASTES: 35-265 NaCl 15 NaOH 0-20 Na₂SO₄ 0-0.01 COPPER
(0-1.0) CHLORINATED HYDROCARBONS (6 PLANTS ONLY)
1 NaOCl 3 NaHCO₃ IN SOLUTION
15 (TO 30) BRINE PURIFICATION MUD: (Mg(OH)₂ CaCO₃ BaSO₄) (TRACE METAL HYDROXIDES) 0.2 FILTER AID 1 NaCl 3 WATER

FIGURE 1. CHLOR-ALKALI MANUFACTURE DIAPHRAGM CELL PROCESS /GRAPHITE ANODES (1).

they contain significant amounts of lead. The Agency currently does not have sufficient information on the concentrations and the migratory potential of the lead in these wastes, but they may be listed as hazardous at some time in the future. Generators, however, must determine whether this waste is hazardous pursuant to §§262.11 of the Subtitle C regulations.

C. Waste Generation and Management (4)

As mentioned previously, chlorinated hydrocarbon contaminants arise primarily from the reaction of chlorine with carbonaceous materials in the graphite anodes. Reaction of chlorine with oils and greases in the equipment and other hydrocarbons present in the system also contributes slightly to the generation of these contaminants. Depending on such variables as the type of liquefaction, quality of anodes and other factors, the chlorinated hydrocarbon contaminants are liquified from the chlorine gas stream during purification in amounts up to 1 kg per kkg of chlorine product.

Management practices vary. Vulcan Materials Co. disposes of the chlorinated hydrocarbon waste by deep well injection, and ICI Americas Ltd. incinerates its waste. Champion International Corp. and PPG Industries, Inc., which landfilled part of their wastes in sealed drums prior to 1977, apparently do not remove the chlorinated hydrocarbon contaminants from the chlorine product at this time. Dow Chemical's management practices are not known.

III. DISCUSSION OF BASIS FOR LISTING

A. Hazards Pose by the Waste

The constituents of the chlorinated hydrocarbon waste include the following (1):

Compound Identified	Weight (%)
chloroform	73.7
carbon tetrachloride	10.8
hexachloroethane	8.0
pentachloroethane	1.3
trichloroethane	1.0
tetrachloroethylene	0.6
dichloroethylene	0.3
1,1,2,2-tetrachloroethane	0.5

Clearly, the waste contains substantial amounts of organic compounds believed to be toxic and carcinogenic. Thus, in light of these constituents' high migratory potential and their ability to persist in the environment, improper management of this waste is likely to lead to substantial hazard.

Many of the constituents of concern have high vapor pressures and thus could pose a substantial hazard to human health and the environment via an air exposure pathway if the waste is improperly managed. Evidence available to EPA's Carcinogen Assessment Group indicates that chloroform, carbon tetrachloride, tetrachloroethylene, and 1,1,2,2-tetrachloroethane are carcinogenic. The Agency believes that the severity of the adverse health effects associated with exposure to these constituents provides a sound basis for listing the waste as hazardous. The high concentration of chloroform alone justifies the listing of this waste as hazardous, in the Agency's judgment. EPA's decision to list the waste is supported further by case histories which reveal that these hazardous constituents can migrate and persist in the environment.

Carbon tetrachloride, a major component of the waste, has been identified in school and basement air in the vicinity of Love Canal (8) and has been implicated in groundwater contamination incidents in Plainfield, Connecticut, where drinking water sources were adversely affected (9). Chloroform has been found in drinking water wells near a Jackson Township, New Jersey landfill in which chemical wastes were dumped, and is also known to have migrated from the Love Canal disposal site (10). Hexachloroethane, another major constituent of the waste of concern, has also migrated from at least one chemical waste disposal site (Table 7.2, Ref. 9). In addition, damage incidents compiled by EPA reveal numerous instances of environmental contamination due to migration of trichloroethane and tetrachloroethylene.(10)

An estimated 125 kkg of waste per year is disposed of in deep wells or by incineration* (2); either method may unfavorably affect human health and the environment by contaminating ground and surface waters or polluting the atmosphere. A deep well injection system that is not properly designed or operated can release hazardous constituents from the well to aquifers used as drinking water sources. Improper incineration of chlorinated hydrocarbons can result in the generation and emission of highly toxic combustion products such as phosgene (5,6,7) and chronically toxic chlorinated aromatic compounds.(15) The remainder of these wastes (up to 180 kkg per year) is disposed of by means not known to the Agency. Landfilling of drummed waste has been practiced in the past. This disposal method presents obvious hazards; drums are likely to corrode in the landfill and release the waste to the surrounding area. Waste constituents could then volatilize and enter the atmosphere or migrate to ground and surface waters.

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*This number was derived by multiplying 90% of the plant nameplate capacity by 0.5, on the assumption that, on average, 0.5 kg of chlorinated hydrocarbon wastes are generated per kkg of chlorine.

Health and Environmental Effects

Chloroform

Chloroform has been identified by the EPA Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Due to its highly volatile nature, (App. B), improper disposal of chloroform-containing wastes may pose an air pollution hazard. Long range exposures have caused both physical and neurological disorders in humans, with liver and kidney toxic responses representing the most prevalent physical pathology. FDA prohibits the use of chloroform in drugs, cosmetics or food contact material. Additional information and specific references on the adverse effects of chloroform can be found in Appendix A.

Carbon Tetrachloride

Carbon tetrachloride (tetrachloromethane) has been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Its toxic effects include neurological damage and damage to the kidney and lungs. It is volatile and slightly soluble in water, and is therefore expected to migrate readily in the environment (11). Additional information and specific references on the adverse effects of carbon tetrachloride can be found in Appendix A.

Hexachloroethane

Hexachloroethane is moderately toxic to humans and is one of the more toxic chlorinated ethanes to aquatic species. It appears to have the potential to bioaccumulate (App. B). Humans exposed to hexachloroethane may suffer central nervous system depression and liver, kidney and heart degeneration. It has also been shown to be carcinogenic to laboratory animals. Little information is available on its environmental fate and transport, but, due to the nature of the adverse affects associated with exposure to this compound, the Agency believes that improper disposal of a waste containing a significant amount of hexachloroethane may pose a hazard to human health and the environment. Additional information and specific references on the adverse effects of hexachloroethane can be found in Appendix A.

Trichloroethane

The trichloroethanes (1,1,1-trichloroethane and 1,1,2-trichloroethane) are toxic to humans and animals, and have been shown or are suspected to be carcinogenic. Because of the toxic and/or carcinogenic effects of these compounds, the Agency believes that improper management of wastes which contain them may pose a hazard to human health and the environment. Additional information and specific references on the adverse effects of trichloroethanes can be found in Appendix A.

Dichloroethylenes

Exposure to dichloroethylenes can result in adverse human health effects. The three isomers appear to have similar toxic effects, including depression of the central nervous system and liver and kidney damage (App. A). Two isomers are mutagenic in bacterial sytems and one isomer has been shown to be carcinogenic in laboratory animals (App.A). Information on environmental fate and transport is scarce but, due to the nature of the health effects resulting from exposure to dichloroethylenes, the Agency has determined that improper management of wastes containing these compounds poses a hazard to human health and the enviroment. Additional information and specific references on the adverse effects of dichloroethylenes can be found in Appendix A.

Tetrachloroethylene

Tetrachloroethylene has been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. In addition, repeated exposure to tetrachloroethylene is implicated in mammalian liver and kidney damage (App.A). Additional information and specific references on the adverse effects of tetrachloroethylene is given in Appendix A.

1,1,2,2-Tetrachloroethane

1,1,2,2-tetrachloroethane has been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Occupational exposure has produced neurological symptoms, liver and kidney damage, pulmonary edema and fatty degeneration of the heart muscle. 1,1,2,2-tetrachloroethane is soluble in water (2900 ppm) and thus has high migratory potential (11). Although environmental fate and transport processes are not well-defined (microbial degradation appears to be the only known degredation mechanism (App. B), and this process is not likely to occur under the abiotic conditions prevailing in most aquifiers), the Agency believes that, due to the severity of the health effects associated with exposure to this compound, improper disposal of the wastes in which it is contained poses a substantial hazard. Additional information and specific references on the adverse effects of 1,1,2,2-tetrachloroethane can be found in Appendix A.

The waste also contains a significant amount of pentachloroethane, a toxic chlorinated organic. At this time the Agency has not compiled data on specific health effects or environmental persistence and mobility; when the data are obtained, a document will be prepared for Appendix A.

REFERENCES

K073: Chlorine Production: diaphragm cell process.

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2. Versar, Inc. Written communication to J. Bellin, U.S. EPA. June 3, 1980.

3. U.S. EPA. Development document for effluent limitations guidelines and standards for the inorganic chemicals manufacturing point source category. EPA No. 440/1-80/007b. June, 1980.

4. U.S. EPA. Draft background document - Chlorinated hydrocarbon bearing wastes from the diaphragm cell process in chlorine production. Prepared by Versar, Inc. for U.S. EPA. Office of Water Planning and Standards. May 21, 1980.

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8. New York State Departement of Health. Love Canal, Public Health Bomb. A special report to the Governor and Legislature. 1978.

9. Acurex Corporation. Chlorinated hydrocarbon manufacture: an overview. Preliminary draft report. February 1980.

10. U.S. EPA. Damages and threats caused by hazardous material sites. EPA No. 430/9-80/004. January 1980.

11. Verschueren, K. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Co., New York. 1977.

Response to Comments: Chlorine Production (Diaphragm Cell Process).

1. One commenter questioned the Agency's characterization of 1,1,1-trichloroethane as a carcinogen. The commenter argues that based on their evaluation of the available data, 1,1,1-trichloroethane has not been found to be carcinogenic (i.e., the commenter believes that the Agency has incorrectly assessed the data).

   The Agency disagrees with the commenter's claim. Although an NCI Bioassay Study on the carcinogenicity of 1,1,1-trichloroethane referred to in the listing background document and an unpublished study are inconclusive, positive responses in two *in vitro* systems (a rat embryo cell transformation assay (Price et. al. 1978) and a bacterial mutation assay (Simmon et. al. 1977; McCann and Ames, 1976)) currently used to detect chemical carcinogens, indicate that 1,1,1-trichloroethane has the potential for carcinogenicity in animals. Additionally, a two year carcinogenesis animal bioassay is being repeated at the National Cancer Institute. Therefore, the Agency believes that there is ample evidence to consider 1,1,1-trichloroethane as a suspect carcinogen.* The listing background document on trichloroethane production and the Health and Environmental Effects Profile on 1,1,1-trichloroethane has been modified to discuss these findings.

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*It should be noted that the Agency recently determined to retain the listing of 1,1,1-trichloroethane as a toxic pollutant under §307(a) of the Clean Water Act. The reasons for that action are incorporated by reference herein.

References

McCann, J. and B. Ames. Detection of Carcinogens as Mutagens in the *Salmonella* Microsome Test. Assay of 300 chemicals. Proc. Nat. Acad. Sci. 78:950:1976.

Price, P.J. et al. Transforming Activities of Trichloroethylene and Proposed Industrial Alternatives. In Vitro 14:290:1978.

Simmon, V.F. et al. Mutagenic Activity of Chemicals Identified in Drinking Water. *In*: Progress in Genetic Toxicology. I.D. Scott, B.A. Bridges and F.H. Sobels, ed. pp.249-258. Elsevier, N.Y., 1977.

SJ40-04
January 1, 1981

LISTING BACKGROUND DOCUMENT

NITROBENZENE/ANILINE PRODUCTION

K083: Distillation bottoms from aniline production (T)

K103: Process residues from aniline extraction from the production of aniline (T).

K104: Combined wastewater streams generated from nitrobenzene/aniline production (T).

I. Summary of Basis for Listing

The first listed waste is the bottom residue generated from the purification of aniline by distillation. The second listed waste results from the extraction step in aniline production and may or may not be combined with other process waters. This listing covers the uncombined waste streams. The third listed waste is the combined process wastewater streams from the co-production of nitrobenzene and aniline. These waste streams all contain toxic nitrogenous organic materials, and the wastewater stream is likely to contain benzene as well.

The Administrator has determined that still bottoms from aniline distillation, process residues from aniline extraction (when generated as a separate waste stream and not combined with other process wastewater streams), and wastewater generated from nitrobenzene and aniline production are solid wastes which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1) The distillation bottoms contain aniline, diphenylamine, nitrobenzene, and phenylenediamine while the combined wastewater stream contains these constituents and usually contains benzene as well. The process residue from aniline extraction, if disposed of separately, contains aniline, nitrobenzene and phenylenediamine. All of these constituents are toxic. Benzene is a known human carcinogen. Aniline, diphenylamine and phenylenediamine are carcinogenic to laboratory animals. Diphenylamine is expected to bioaccumulate.

2) Total potential loadings of benzene and aniline in the wastewater stream from the production of nitrobenzene and aniline could be as high as 9.5 kkg and 150 kkg annually, quantities believed by the Agency to be quite significant in view of these compounds' adverse health effects.

3) Current disposal practices of these wastes are not well documented. However, there is a high potential for contaminating groundwater by leaching from waste treatment lagoons or landfills that are not properly designed or operated, since these constituents have high migratory potential, and some have proven mobile and persistent in actual waste management practice. In addition, under certain conditions, release to the atmosphere by volatilization poses a risk of inhalation of aniline and nitrobenzene.

4) In a damage incident involving improperly managed aniline distillation bottoms, waste oils were contaminated with nitrobenzene from the distillation residues and spread over roads, posing the risk of human exposure to dangerously high concentrations of nitrobenzene. This waste has thus proven capable of posing a substantial hazard in actual waste management practice.

5) The State of Texas regulates distillation bottoms from aniline production as a hazardous waste.

II. Sources of the Waste and Typical Disposal Practices

A. Profile of the Industry

Nitrobenzene and aniline are major chemical intermediates; the actual nameplate capacity was reported as 557,000 kkg(25) and 313,000 kkg, respectively.(2) The U.S. International Trade Commission lists aniline as the sixth largest volume intermediate in terms of 1978 production.(1) Table 1 lists the facilities producing nitrobenzene and aniline, and their production capacities. As is indicated, most facilities produce both nitrobenzene and aniline. In 1978 97% of nitrobenzene produced was used for the synthesis of aniline.(2,25) The balance is purified for use chiefly as a solvent, or in the manufacture of pharmaceuticals, dyes and photographic chemicals.

United States production of aniline is increasing. Production levels were 151,000 kkg in 1969, 186,000 kkg in 1972, 187,000 kkg in 1975,(3) and 270,000 kkg in 1978.(1) Aniline production capacity is anticipated to reach 450,000 kkg in 1980. Most aniline (about 40%) is used for the production of polymeric methylene phenylisocyanate, an intermediate used in the manufacture of urethanes; another 35% is used in the synthesis of rubber chemicals.(2) The remainder is mainly used in the manufacture of dyes and drugs.

Table 1

PRODUCER LOCATIONS AND PRODUCTION CAPACITIES

MANUFACTURER	FACILITY	PRODUCTION CAPACITY (10^3kkg) 1978 Nitrobenzene(25)	1977 Aniline(2)
American Cyanamid Co.	Bound Brook, NJ	48	27
American Cyanamid Co.	Willow Island	33	28
E. I. Dupont de Nemours & Company, Inc.	Beaumont, TX	140	104
E. I. Dupont de Nemours & Company, Inc.	Gibbstown, NJ	90	59
First Mississippi Corp.	Pascagoula, MS	151	45
Mallinkrodt Corp.	Raleigh, NC	0	10
Mobay Chemical Corp.	New Martinsville, WV	61	45
Rubicon Chemicals, Inc.	Geismar, LA	34	27
		557	340

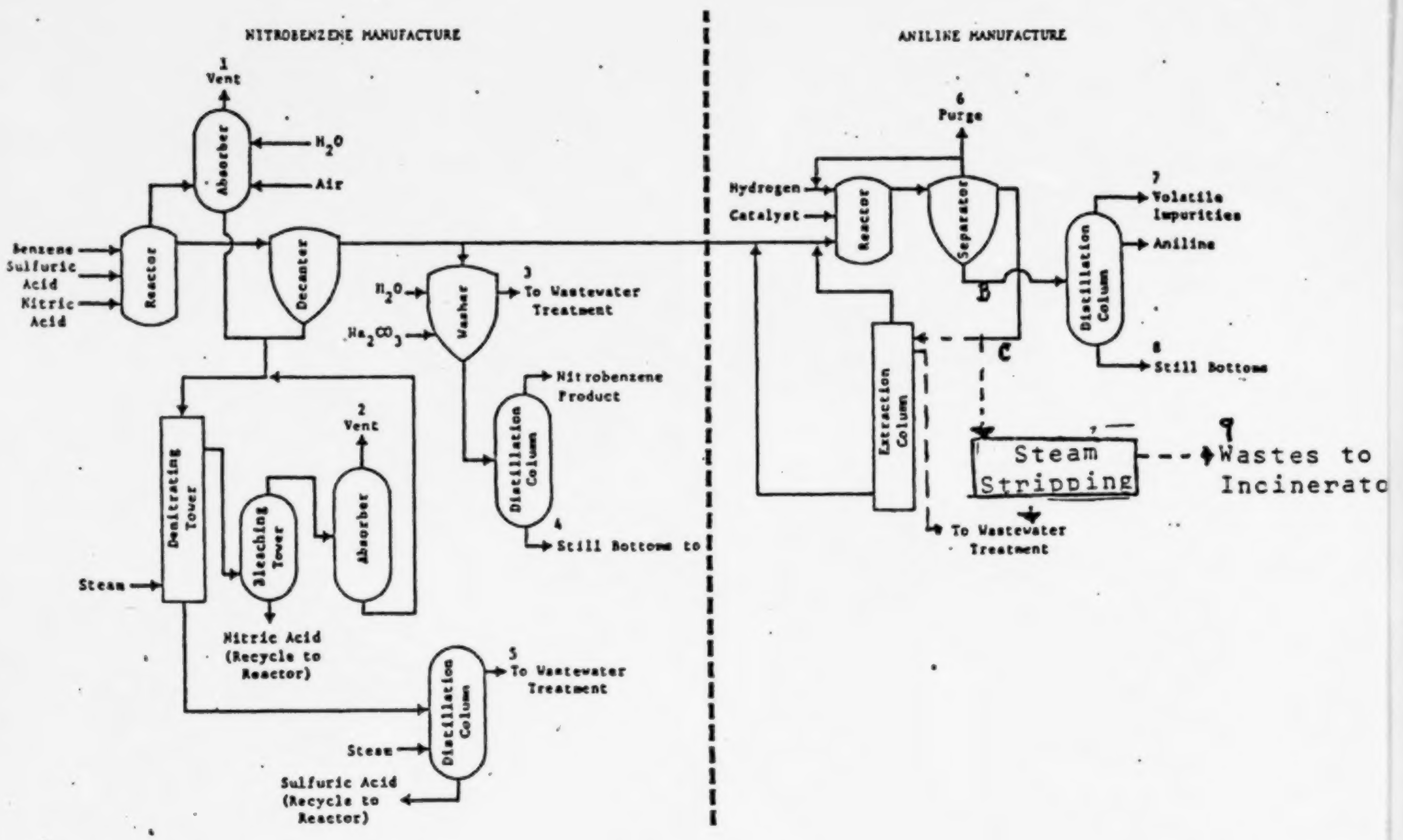
B. Manufacturing Process(2)

1. Manufacture of Nitrobenzene

Nitrobenzene is made by the direct nitration of benzene using a sulfuric-nitric acid mixture. In the most common continuous phase process, benzene is nitrated with an aqueous mixture of sulfuric acid (53 to 60 mole percent) and nitric acid (32 to 39 mole percent) at atmospheric pressure and temperatures between 45 to 90°C. Yields are typically better than 98 percent. This process (see Figure 1) is carried out in vented stainless steel vessels equipped with high speed agitators and cooling coils. Average residence time is approximately 8 to 10 minutes. Nitrobenzene is continuously drawn from the side of the reactor and separated in a decanter. Once separated, this "crude" nitrobenzene is reportedly used directly in the manufacture of aniline.

If pure nitrobenzene is required, the product is washed first with water and subsequently with an alkaline solution (generally either a sodium carbonate or sodium hydroxide solution) in small vessels equipped with high speed mechanical agitators, and then distilled. The wastewater resulting from the washing operation (stream 3 in Figure 1), is one component of the waterborne waste stream of concern in this document.

FIGURE 1
SIGNIFICANT POLLUTANTS FROM
NITROBENZENE/ANILINE MANUFACTURE (MODIFIED FROM (2))


NITROBENZENE MANUFACTURE
ANILINE MANUFACTURE
1
Vent
Absorber
H_2O
Air
Benzene
Sulfuric Acid
Nitric Acid
Reactor
Decanter
H_2O
Na_2CO_3
Washer
3
To Wastewater Treatment
Nitrobenzene Product
Distillation Column
4
Still Bottoms to
2
Vent
Denitrating Tower
Bleaching Tower
Absorber
Steam
Nitric Acid (Recycle to Reactor)
5
To Wastewater Treatment
Distillation Column
Steam
Sulfuric Acid (Recycle to Reactor)
6
Purge
Hydrogen
Catalyst
Reactor
Separator
B
7
Volatile Impurities
Aniline
Distillation Column
8
Still Bottoms
C
Extraction Column
Steam Stripping
9
Wastes to Incinerato
To Wastewater Treatment

Point 1*
Benzene, Nitroalkanes, Nitrobenzene, Nitrogen Oxides

Point 2*
Benzene, Nitroalkanes, Nitrobenzene, Nitrogen Oxides

Point 3
Benzene, Benzoic Acid, Carboxylic Acids, Nitrates, Nitrites, Nitrobenzene, Nitrophenol

Point 4**
Dinitrobenzene, Nitrobenzene, Nitrophenol, Nitrogen Containing High Molecular Weight Polymers, Polycarboxylic Acid, Dinitrotoluene

FIGURE 1 CONTINUED

Point 5
Benzene, Nitrobenzene, Nitrophenol, Polycarboxylic Acid, Nitrogen Containing High Molecular Weight Polymers

Point 6*
Aniline, Carbon Monoxide, Hydrogen, Meth~~e~~ane, Nitrobenzene

Point 7*
Cyclohexylamine, Volatile Amines, Water

Point 8*
Aminophenols, Azepins, Diphenylamine, Nitrobenzene, Phenylenediamine, Nitrogen Containing High Molecular Weight Polymers

Point 9
Aminophenol, Aniline, Nitrobenzene, Phenylenediamine, Water Soluble Amines

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* Emitted to air and therefore not subject to RCRA.
**This waste was listed in the May 19, 1980 promulgation (see "Nitrobenzene Background Document" for details).

Recovery of spent acid is essential from the standpoint of economical operation. Generally, unreacted nitric acid is extracted from the spent acid by steam stripping (denitrating tower). The bottom product, dilute sulfuric acid (60 percent by weight), is then concentrated by distillation (sulfuric acid concentrator) and recycled to the reactor as shown, or used in other manufacturing operations. Nitric acid removed overhead from the denitrating tower is bleached with air to remove nitrogen oxide and subsequently recycled to the reactor. The overhead nitrogen oxides from the bleacher are scrubbed with water and recycled to the denitrating tower.*/ The waste resulting from acid recovery (number 5 in Figure 1) is another component of the aqueous waste stream of concern in this document.

2. Production of Aniline(2,3)

In the U.S., aniline production is based almost exclusively on vapor phase reduction of nitrobenzene in the presence of a copper catalyst. This process is also illustrated in Figure 1. With the exception of one facility (Mallinkrodt, Inc.), the nitrobenzene feedstock is produced on site.(2) The nitrobenzene is vaporized in a stream of hydrogen and introduced into the reactor. The crude product mixture (aniline, hydrogen and water) leaving the reactor is condensed and separated from the gas stream. Most of this gas stream is compressed and recycled to the reactor, but, to prevent build-up of gaseous impurities in the reactor, some gas is purged. The two-phase (aqueous and organic) reactor product mixture is separated. The lower organic phase (stream B, Figure 1), consisting principally of aniline, up to 5 percent nitrobenzene, and 5 percent water,(2) is purified by two stage distillation. In the crude still, aniline and water are removed overhead, while higher boiling organic impurities, such as nitrobenzene, remain in the still bottoms (noted as 8, Figure 1). In a finishing distillation step, the overhead product from the crude still is purified to 99% specification, and the bottoms from this finishing distillation step are combined with the crude distillation bottoms. (This process is shown as a single distillation in Figure 1.)(3)

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*Another approach to spent acid recovery uses benzene, rather than steam, to strip nitric acid from spent acid in the denitrating tower. The nitric acid is thus dissolved in the benzene and fed to the reactor. The remaining sulfuric acid is concentrated as before.

Several methods are used to recover aniline from the aqueous phase of the separator (C in Figure 1). Aniline may for instance be concentrated from this stream by steam stripping. The resulting enriched aniline/water mixture is then incinerated. This latter waste stream is not included within the present listing, although it may be listed in the future. The Agency solicits information as to the composition of this waste and risks associated with its improper disposal.

At some facilities aniline is recovered by countercurrent extraction with nitrobenzene. Recovered aniline and nitrobenzene are recycled to the reactor. In either case (i.e., if either extraction or steam stripping is used), the residual waste stream (9 in Figure 1) ordinarily is directed to wastewater treatment with other process wastewater streams. This is the third component of the waterborne waste stream of concern in this document. In some facilities, the residues from the extraction step are not combined with other process wastewaters. In such cases, the listing includes the separate wastewater stream from the extraction step.

C. Waste Generation and Management

The listed wastes consist of still bottoms from the distillation of aniline (Point 8, Figure 1) and the wastewater streams generated from nitrobenzene/aniline manufacture (points 3, 5 and 9 of Figure 1), which are most often combined before wastewater treatment. (Wastes from the aniline extraction step are listed when disposed of separately, as discussed above.)

On the basis of process chemistry assumptions set forth in (2), the aniline distillation bottoms are expected to contain nitrobenzene, nitrophenols, aniline, diphenylamine, and phenylenediamine. While precise concentrations are unknown, concentrations of nitrobenzene are expected to be quite high, since the organic phase prior to distillation consists of 5 percent nitrobenzene, most of which would be expected to be (and is intended to be) removed by distillation, leaving wastewater with low levels of nitrobenzene to go to treatment.

The volume of aniline still bottoms and the present practices of the industry with regard to their disposal are not well defined. The most common disposal method for distillation bottoms is storage in drums in private landfills.(27) Some of these wastes are apparently utilized for their acid-neutralizing capacity in drilling operations.(4)

The wastewater stream components from nitrobenzene/aniline manufacture include: the nitrobenzene washwater (Point 3), the acid distillation column overhead (point 5) and the aniline recovery stream (point 9). Based on a knowledge of process chemistry, these streams are estimated to contain the pollutants indicated in Figure 1. Most manufacturers combine these wastewater streams prior to treatment.(2) Table 2 lists typical concentrations of selected pollutants found in combined nitrobenzene/aniline waste streams, as reported by two manufacturers.(2)

A variety of wastewater treatment methods are applied, and it is not known to what extent these are successful in removing the toxic chemicals from the listed waste. The following treatment methods have been reported:(2) steam stripping, carbon adsorption, aerated lagoon, biological contact stabilization, clarification, equalization, activated sludge, stabilization pond, land application, and subsurface disposal.

Table 2

Characterization of Raw Waste Loading From Nitrobenzene/Aniline Manufacture(2)

	kg/kkg aniline product			kkg/yr*
	Avg.	Min.	Max.	Max.
Aniline	0.067	0.005	0.49	150
Benzene	0.005	0	0.031	9.5
Nitrobenzene	0.002	0	0.012	3.7

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*Obtained by multiplying the maximal value by the 340,000 kkg by 90% of annual aniline nameplate production capacity (since plants rarely operate at 100% of capacity).

In addition to the above pollutants whose identity was quantitatively confirmed, animophenol, benzoic acid, nitrophenol, and phenylene diamine as well as nitrates and nitrites are estimated(2) to occur. Of these constituents the wastewater loading data show that at least aniline, benzene and nitrobenzene are present in substantial concentrations, and generated in significant quantities annually.

As noted above, the wastewaters from the extraction step of aniline production are not always combined with other process wastewater streams.

III. Discussion of Basis for Listing

A. Hazards Posed by the Waste

On the basis of available information, it is apparent that the listed wastes contain toxic organic materials, including nitrobenzene, aniline, diphenylamine and phenylenediamine, and (for the combined wastewaters) benzene. These constituents are all toxic, and all but nitrobenzene are experimental or (in the case of benzene) known carcinogens. All of these constituents are projected to have migratory potential and to be mobile and persistent in ground and surface water (Appendix B), so that they can create a substantial hazard if disposal facilities are not properly designed and operated. Aniline, nitrobenzene and phenylenediamine are quite soluble (solubility 34,000, 38,000 ppm and 1900 ppm respectively),(5) and thus can easily migrate through dry sandy soils. Diphenylamine is also significantly soluble for purposes of risk of chronic exposure (300 ppm (6)). Furthermore, the solubility of amines such as aniline, diphenylanime and phenylendiamine increases significantly under conditions which are more acidic than their acid dissociation constant (pKa is 6.0 for phenylenediamine). Since the pH of the rainfall in the United States presently ranges from 4.0 - 5.0(9,22), residues of aniline and phenylenediamine can be expected to leach to surface and groundwater if these wastes are improperly transported, treated, stored, disposed of, or otherwise managed.

Present waste disposal practices may be inadequate to prevent waste migration. Certainly, improper management may result in release of harmful constituents, particularly in view of the properties of the waste constituents as described above. For instance, if this waste should be exposed to an environment subject to acid rainfall, disposed residues containing phenylenediamine contacted by acid rainfall can be expected to leach and to migrate to surface and groundwater.

Further, if this waste is treated in a lagoon, even under relatively mild environmental conditions, the harmful constituents can be expected to leach from the waste, as a result of their moderate to extreme water solubility properties if the lagoon is not properly designed or operated.
Once released from the matrix of the waste, these constituents could migrate from the waste and contaminate groundwater. Nitrobenzene, for example, has proven mobile and persistent in two major damage incidents involving waste disposal at the Monsanto Chemical dump in East St. Louis and at the LaBounty dump in Charles City, Iowa.(10)

Another potential hazard associated with lagoon treatment of this waste would be the volatilization of compounds with appreciable vapor pressure such as benzene into the atmosphere, thus posing a hazard via inhalation. Benzene has proven capable of migration and persistence via an air exposure pathway in many actual damage incidents, Love Canal being the most notorious.

If the wastes are landfilled, even in plastic-lined drums, they can create a potential hazard. All drums have a limited life span, for the exterior metal corrodes in the presence of even small amounts of moisture. When this occurs, the potential for groundwater contamination is high if the landfill is not properly designed or operated. It should be noted that many of the subject production facilities are located in regions of significant rainfall (LA, NJ, WV), so that ample percolating liquid is available for leachate formation. (In any case, there is no reason to believe that wastes will be containerized at all, since, absent Subtitle C regulation, wastes could be landfilled in a variety of improper ways.)

A special hazard posed by the subject wastes is the possibility of the formation over time of highly carcinogenic nitrosamines from some of their constituents.(2) Aniline and other amines (most importantly secondary amines) as well as nitrites are thought to be present in these wastes (Figure 1). These substances may react to form nitrosamines, especially under acidic conditions. Such conditions might result as a consequence of co-disposal of the listed wastes with acidic wastes, or under conditions of continued acid rainfall.

Improperly managed aniline distillation bottoms have been involved in at least one damage incident.(23) From 1976 through November 1978, contaminated waste oils were used as dust suppressant on roads throughout East Texas. The chief source of contamination were aniline tars (still bottoms) from aniline production*, generated by Dupont's Beaumont facility. These still bottoms were sent to Browning-Ferris Industries Chemical Services, Inc., a state permitted waste management facility, which proceeded impermissibly to mix the wastes with waste oil, which oil was used indiscriminately as a road dust supressant. Nitrobenzene levels in contaminated soil varied, and were as high as 21,000 ppm. Most of the concentrations were deemed by state environmental officials as more than sufficient to cause substantial harm. The danger was discovered before occurence of known harm, and Browning-Ferris was ordered to remove approximately 10,000 cubic yards of contaminated material from one subdivision, and additional amounts of material from four additional subdivisions.(23)

This incident not only illustrates the potential for substantial harm if this waste is disposed of improperly, but also suggests strongly that the aniline distillation residues may contain very high concentrations of nitrobenzene, in light of the substantial concentrations found in the contaminated road oil. Furthermore, aniline distillation bottoms are regulated as hazardous wastes (termed 'Class I wastes' under the state waste management system) by the State of Texas (23), another indication of their potential for hazard.

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* The waste oils were heavily contaminated with nitrobenzene, and the only source of nitrobenzene in wastes accepted by Browning-Ferris were aniline distillation wastes. (23 at p. 17.)

B. Health and Ecological Effects

Benzene

EPA's Carcinogen Assessment Group has designated benzene as a human carcinogen (leukemogen). Acute exposure to high concentrations of benzene causes central nervous system depression (euphoria, nausea, staggering gait and coma). Inhalation of lower amounts produces dizziness, headache and nausea. Benzene has demonstrated teratogenic effects in laboratory animals. Chromosomal changes have also been demonstrated in workers exposed to benzene.(28)

For maximum protection of human health from the potential carcinogenic effects of exposure to benzene through ingestion the ambient water criterion is 0.80 ug/1(29).

Because benzene is soluble in water, it could be leached from the wastewater treatment sludge which would be generated from treatment of the combined wastewaters, in a landfill situation and pose a threat to groundwater supplies. Because it is also volatile (vapor pressure = 100 mm at 26.1°C (Appendix B.)), it may pose an inhalation hazard during handling in transportation and disposal. Additional information and specific references on the adverse health and environmental effects of benzene can be found in Appendix A.

Nitrobenzene

Nitrobenzene has toxic reproductive effects: in rats it delays embryogenesis, alters normal placentation, and produces abnormal fetuses (14); changes in the tissues of the chorion and placenta have been reported in women exposed to nitrobenzene (15). Nitrobenzene has been listed as a Priority Pollutant in accordance with §307(a) of the Clean Water Act of 1977.

With present data, it is not possible to fully estimate its aquatic fate. Hydrolysis and volatilization from water are considered unlikely (15). Adsorption onto humus and clay, and subsequent production by weathering and biological action, of (carcinogenic) benzidine and diphenylhydrazine could be a major fate pathway (12) Nitrobenzene is neither stored nor ecologically magnified, but is resistant to degradation by soil microflora (11, 12). In mammalian systems nitrobenzene is metabolized to aniline, nitrophenol, p-hydroxyaniline and other metabolites, which are excreted in urine, but such metabolism in man is slower by an order of magnitude than in animals (13).

The criterion to protect freshwater aquatic life is 480 ug/l (24 hour average). The occupational exposure limit (OSHA) is 5 mg/m^3 (skin, 8 hr TWA). The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit for industrial exposure to nitrobenzene is 1 ppm.(23)

Additional information and specific references on the adverse health effects of nitrobenzene can be found in Appendix A.

Aniline

Aniline is an experimental carcinogen (16). Its absorption causes anoxia due to the formation of methemoglobin, but significant chronic problems (other than animal carcinogencity) have not been demonstrated. Human exposure to vapor concentrations of 7-50 mm has been observed to cause slight symptoms.(30) Rapid absorption through the intact skin is frequently the route of entry.(18,30) Cyanosis is the most prominent outward symptom of aniline intoxication.(8) At 0.4 mg/l aniline is toxic to Daphnia (8). OSHA's PEL for aniline is 19 mg/m^3 (skin, 8 hr TWA)(17). Additional information and specific references on the adverse health effects of aniline can be found in Appendix A.

Phenylenediamine

Phenylenediamine is a highly toxic substance, continued exposure to which can cause liver injury (18). It is a suspected carcinogen and teratogen (18). Of the three isomers, the *p*-substituted compound is by far the more toxic (19). The relative concentrations of the isomers in the listed waste are not known. The oral toxicity for human beings is high (LD_{lo}= 50 mg/kg (19)), which, in combination with the high water solubility of this compound is worrisome. Phenylenediamine is listed by DOT as a hazardous substance (ORM-A), and the OSHA PEL is 0.1 mg/m^3(8 hr TWA) (17).

Diphenylamine

Diphenylamine is an experimental carcinogen and teratogen (19). Chronic exposure to diphenylamine induces cystic lesions in the chicken(20) and the rat.(24) The American Conference of Industrial Hygienists has established 10 mg/m^3 as an acceptable TLV for occupational exposure (21). Diphenylamine can also be expected to bioaccumulate, due to its high octanol/water partion co-efficient of 2,200 (7).

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Response to Comments: Distillation Bottoms, Wastewater Treatment Streams and Process Residues from Nitrobenzene/Aniline Production.

One commenter, a manufacturer of these chemicals, objected to the listing of wastewater streams from nitrobenzene/aniline production, noting that they fully pre-treat these wastewater streams, removing nitrobenzene, benzene and aniline to extremely low levels, apparently taking issue with the Agency's determination that these wastes generally contain appreciable levels of these (and other) toxic chemicals. The commenter went on to state that the mismanagement incident (cited in the BD) regarding distillation bottoms from the production of nitrobenzene in fact involved waste nitrobenzene,rather than the listed waste.

We are not persuaded by this comment that the listed wastes typically and frequently contain inconsequential levels of hazardous constituents. To the extent an individual facility is able to remove or reduce the constituents of concern by a treatment process, the May 19, 1980 regulations provide explicit procedures which a generator may employ to petition the Administrator to amend part 261 to exclude a listed waste produced at a particular facility. (See §§ 261.20 and 260.22). a particular facility are set forth in §§261.20 and 260.22. The commenter can use these procedures to petition for removal of the subject streams at its facility. However, in the absence of proof regarding error in its assumptions concerning the nature and concentration of toxicants, and the amounts of these hazardous wastes generated, the Agency will continue to list these streams as hazardous wastes. It should also be noted that two of the toxic constituents of concern (phenylene diamine and diphenylamine) were not adressed by the commenter, thus, no data was provided to refute their prersence or potential for creating a hazard.

With regard to the demonstrated potential for mismanagement of these wastes, the cited legal testimony implicated aniline distillation wastes (ref. 23 of BD at p. 17, citing aniline tars, not waste nitrobenzene, as the waste mixed with the road oil).

The Agency therefore disagrees with the commenter, and judges that, because of the toxic nature of many of the components of these wastes, the large amount of wastes generated, and the demonstrated potential for mismanagement, these wastes may pose a substantial present or potential hazard to human health or the environment, and that they should be subject to appropriate management requirements.

LISTING BACKGROUND DOCUMENT
VETERINARY PHARMACEUTICALS

K084: Wastewater treatment sludges generated during the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds (T).

K101: Distillation tar residues from the distillation of aniline-based compounds in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds (T).

K102: Residue from the use of activated carbon for decolorization in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds (T).

I. SUMMARY OF BASIS FOR LISTING.

Treatment of wastewater from the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds generates a wastewater treatment sludge containing arsenic or organo-arsenic compounds. The production of this class of veterinary pharmaceuticals also generates residues from the distillation of aniline-based compounds, and from the use of activated carbon for decolorization, which also contain arsenic or organo-arsenic compounds, wastes which are listed in this document.

The Administrator has determined that these wastewater treatment sludges and other arsenic-containing wastes from the production of veterinary pharmaceuticals are solid wastes which pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and, therefore, should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1) These wastes have been shown to contain high concentrations of arsenic. Arsenic is highly toxic and has been identified by the Agency as a substance which has demonstrated substantial evidence of being carcinogenic. It is also a bacterial mutagen, and is teratogenic to laboratory animals.

2) Disposal of these wastes in improperly designed or operated landfills has resulted in arsenic contamination of ground and surface water, providing empirical proof that the arsenic in this waste is soluble and may migrate from disposal sites into soil, groundwater and surface water in concentrations sufficient to create a substantial hazard. Further, since arsenic is an element, and does not degrade with time, it persists, and any contamination caused by mismanagement of these wastes will be long-term.

3) These wastes are generated in large quantities, so that large amounts of arsenic are potentially available for environmental release, an additional hazard posed by this waste.

II. SOURCES OF THE WASTE AND TYPICAL DISPOSAL PRACTICES

A. Profile of the Industry

Three domestic companies currently produce veterinary pharmaceuticals containing arsenic: Salsbury Laboratories in Charles City, Iowa; Whitmoyer Laboratories in Meyerstown, Pennsylvania; and Fleming Laboratories in Charlotte, North Carolina.(1,2)

B. Manufacturing Process and Waste Generation

The manufacture of arsenic-containing pharmaceuticals requires the reaction of an organic compound with inorganic arsenic to form the organic arsenical product, and generates arsenic-containing solid wastes*/

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*/The Agency is aware that these wastes also contain other substances of concern. They contain large quantities of the toxic compounds 1,1,2 trichloroethane, phenol and nitrophenol, as well as o-nitroaniline.(1) 26 organic compounds have been identified in the process waste water in substantial concentrations including 22 priority pollutants.(1) Upon further study and evaluation these wastes may be amended in the future to include these toxic constituents of concern, if this is deemed to be advisable.

Arsenic-containing solid wastes generated during the production process include tars from the distillation of aniline-based compounds, and residue from the use of activated carbon in the decolorization of pharmaceuticals.(4,5) Whitmoyer reported that it generates these wastes in annual quantities of one hundred 55-gallon drums and more than six hundred 55-gallon drums, respectively.(4) Salsbury Labs also generates arsenic-containing tars from production processes.(5)

Production of veterinary pharmaceuticals from arsenic compounds generates wastewaters which contain organic and inorganic arsenic. Treatment of these wastewaters produce arsenic-bearing sludges. Figure 1 is a simplified representation of the wastewater treatment system of one manufacturer's facility: Salsbury Laboratories, which produces organic arsenicals marketed as feed additives for chickens, turkey and swine.(1) Process wastewaters at Salsbury are partially segregated into two sewer systems. The first sewer system (A in Figure 1) carries waste acid washwater (approximately 10,000 gallons per day) from the nitration processes; this washwater is neutralized and clarified. Although this drain system is intended to receive non-arsenic contaminated waste water, adequate separation of arsenic wastes has not been achieved. The acid washwater stream contains approximately 4 kg of arsenic per day.(29) */ Since waste water treatment is claimed

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*/ In the July 16 version of this background document, the Agency stated erroneously that the sludges resulting from treatment of the acid process wastewaters were a separate waste stream, and did not contain significant concentrations of arsenic. This error is

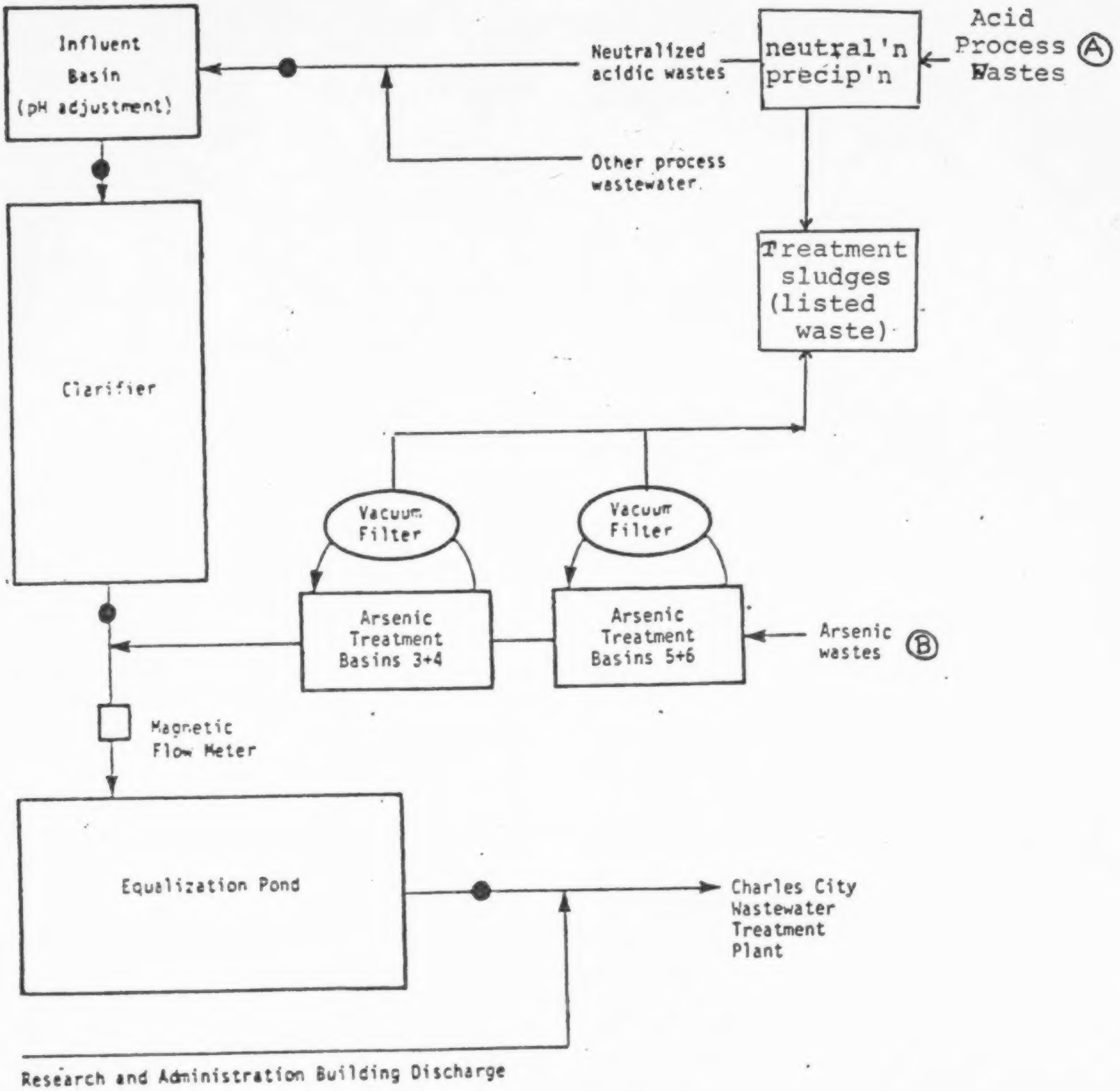
Influent Basin (pH adjustment)
Neutralized acidic wastes
neutral'n precip'n
Acid Process Wastes Ⓐ
Other process wastewater
Treatment sludges (listed waste)
Clarifier
Vacuum Filter
Vacuum Filter
Arsenic Treatment Basins 3+4
Arsenic Treatment Basins 5+6
Arsenic wastes Ⓑ
Magnetic Flow Meter
Equalization Pond
Charles City Wastewater Treatment Plant
Research and Administration Building Discharge

FIGURE 1: Salsbury Wastewater Treatment Facility (adapted from ref. 25).

(72)

to be 99% effective(27), the treatment sludges resulting from this acid washwater will contain almost all of this arsenic loading.

The second sewer system (B in Figure 1), collects about 25,000 to 30,000 gallons per day of arsenic-containing process wastewaters which originate from the manufacture of Salsbury's arsenical compounds, such as 3-nitro-4-hydroxyphenylarsonic acid and 4-nitrophenylarsonic acid. The treatment of this waste stream is operated on a batch basis as a two stage process involving neutralization with slaked lime, the addition of a flocculant, treatment with $MnSO_4$, and two filtration steps. The resulting sludges, containing about 1.6 kg of arsenic per day, are combined with those formed from the treatment of waste stream A. The mixed treatment sludges constitute the first listed waste of concern in this document.

The other manufacturers of arsenic-containing veterinary pharmaceuticals also produce arsenic sludges. Whitmoyer Laboratories generates approximately 1,260 drums per year of sludge from the evaporation, volume reduction and centrifugation of waste salt solutions.(4) Fleming Laboratories reported the production of arsenic sludges, but did not describe the process by which they are generated (24).

The wastewater treatment sludges contain large amounts of arsenic. One sample of fresh sludge from the Salsbury Laboratories disposal site, the LaBounty landfill contained 28,000 ppm of arsenic (see below). In addition, the fact that significant concentrations have been released from the waste at the LaBounty site indicates that the contaminant is present in these wastes in substantial amounts. Borings from soils underlying the arsenic-containing solid waste deposits at the landfill contain a mean arsenic concentration of 700 ppm, and borings from surrounding soils exhibited a mean concentration of 2200 ppm.(1) Samples obtained from a well located between the site and the river showed an arsenic concentration of 590 ppm in groundwater.(1)

The Agency, at present, has no detailed flow process information concerning the manner in which the other listed wastes are generated. However the wastewater treatment sludges generated at Whitmoyer's laboratories are reported to contain 1-7% arsenic.(4)

Arsenic concentrations in the other two listed wastes are also substantial: distillation tars are reported to contain 10-15% arsenic, and residues from activated carbon decolorization are reported to contain 4-14% arsenic.(4)

C. Waste Management

From 1953 to December 1977, Salsbury Laboratories disposed of its solid wastes in the LaBounty Dump, located on the west bank of the Cedar River. (1) Prior to 1953, solid wastes were disposed of across the river at the municipal dump, but quantities are estimated to be relatively minor compared to those at the LaBounty site. The wastewater treatment sludge presently is stored in drums and shipped by rail to Waste Management, Inc., a commercial disposal operation in Livingston, Alabama.(3)

Whitmoyer Laboratories' treatment sludges were stored in on-site lagoons until groundwater contamination was detected (this was also the disposal practice under prior ownership). Off-site disposal has been utilized since that time. Since 1975 Whitmoyer Laboratories has drummed all of its arsenic-containing wastes, and has shipped them to landfills specially designed to impede release of hazardous constituents to the environment.(4) The Agency has no information concerning the current disposal practices of Fleming laboratories.

III. DISCUSSION OF BASIS FOR LISTING

A. Hazards Posed by the Waste

These treatment sludges, distillation tars, and activated carbon residues contain high concentrations of arsenic, an extremely toxic substance. Arsenic and arsenic compounds have been identified by the Agency as a substance which has demonstrated substantial evidence of carcinogenicity. Arsenic is mutagenic to bacteria and teratogenic to laboratory animals. See Section B (Health and Ecological Effects) of this listing background document and Appendix A for further information.

It is quite obvious that improper management of these wastes can result in substantial hazard, since substantial harm has in fact occurred from their faulty management. The most notorious example of this damage occured at the LaBounty landfill.

Various wastes, including large amounts of arsenic sludges, were disposed of at the LaBounty site. In January, 1978 approximately 7.5 cubic meters of arsenic sludge were disposed per day. (1) At one time it was estimated that the site contained more than six million pounds of arsenic(1). The site is located over a major aquifer. As noted above, substantial arsenic contamination of soil and groundwater resulted when the arsenic compounds leached from the waste site. As a result of surface run-off and groundwater discharge, the Cedar River picked up an average load of 53 kg of arsenic per day in the vicinity of the LaBounty Site.(1) The Iowa Department of Environmental Quality issued an order that required Salsbury to cease disposal of wastes at the LaBounty landfill. (77-DQ-01, Dec. 14, 1977). A report on this damage incident concluded that arsenic in the wastewater treatment sludge is "fairly easily solubilized even if it is precipitated with calcium as the arsenate".(5) The presence of arsenic in ground and surface waters in the vicinity of the LaBounty Site likewise clearly indicates that, once released from the waste, it is highly mobile and persistent.

The migratory potential of the arsenic contained in these wastes is also substantiated by the groundwater contamination resulting from the storage of the listed waste and similar wastes by Whitmoyer Laboratories in holding lagoons (4). When the groundwater contamination was discovered in the late 1960's, the company began disposing of the sludges at a number of different sites; presently, these wastes are transported by truck to hazardous waste landfills or a specially designed vault disposal operation (4). Again, this demonstrates the potential hazard posed by the migration of waste constituents from a disposal site and the generator's subsequent recognition of this hazard.

An additional demonstration of the necessity for proper management occurred when Salsbury Laboratories, as a result of a cease order, began disposing of solid wastes in a temporary on-site holding basin.(1) This disposal method was quickly terminated because leachate was detected in the underdrain system within 24-hours after disposal.(1) The 1977 court action, coupled with the present management of these wastes in chemical waste landfills, substantiates the concern by both the state and the generator for the proper management and disposal of this hazardous waste.

These damage incidents show that arsenic may easily migrate from these wastes and persist in the environment upon release. Indeed, because arsenic is an element, and does not degrade with the passage of time, it will persist in some form virtually indefinitely.

There are a number of additional reasons to impose hazardous waste status on this waste. Unregulated transportation of this waste to off-site disposal facilities increases the likelihood of harmful exposure to human beings and the environment. Without proper means to track the waste from the point of generation to its ultimate destination, the waste might not reach its designated destination at all, thus making it available to do harm elsewhere.

Furthermore, as previously indicated, arsenic sludges from the production of veterinary pharmaceuticals are generated in very substantial quantitites (in January 1978, approximately 7.5 m^3/day were generated at the Salsbury plant alone (1)). Large amounts of arsenic are thus available for potential environmental release, posing the danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time, since large amounts of this pollutant are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or exhausted due to the large quantities of pollutant available. All of these considerations increase the possibility of exposure to this harmful constituent.

B. Health and Ecological Effects

Health Effects

Arsenic is acutely toxic to animals and humans (6). Death in humans has occurred following ingestion of very small amounts (5mg/kg) (7). Several epidemiological studies have associated cancers with occupational exposure to arsenic (8-10), including those of the lung, lymphatics and blood (11,12). Skin cancer has been associated with the presence of arsenic in drinking water (13), while liver cancer has developed in several cases following ingestion of arsenic (14). The human carcinogenic potential of arsenic is supported by animal studies. arsenic and its compounds have been identified by the Agency as demonstrating substantial evidence of carcinogenicity.

Occupational exposure to arsenic has also resulted in chromosomal damage (15), and several different arsenic compounds have demonstrated positive mutagenic effects in laboratory studies (16-18). The teratogenicity of arsenic and arsenic compounds is well established (19-21); observed defects include those of the skull, brain, kidneys, gonads, eyes, ribs and genitourinary system.

The effects of chronic arsenic exposure include skin diseases progressing to gangrene, liver damage, neurological disturbances (22), disturbances in red blood cell production and cardiovascular disease (8).

Additional information and specific reference on adverse effects of arsenic can be found in Appendix A.

Ecological Effects

The data base for the toxicity of arsenic to aquatic organisms is more complete for freshwater organisms; concentrations as low as 128 ug/l are acutely toxic to freshwater fish. Based on one chronic life cycle test using Daphnia magna, a chronic value for arsenic was estimated at 853 ug/l (21).

Regulatory Recognition of Hazard

OSHA has set a standard 8-hr air TWA in air of 0.5 mg/m^3 for occupational arsenic exposure. 0.05 mg/m^3 has been proposed for arsenic trioxide (23). DOT requires a "poison" warning label.

EPA's Office of Toxic Substances under FIFRA has issued a pre-RPAR. Arsenic is designated as a priority pollutant under Section 307(a) of the CWA. The Office of Drinking Water has regulated arsenic under the Safe Drinking Water Act and the Office of Air Quality Planning and Standards has begun a preregulatory assessment of arsenic based on its suspected carcinogenic effects. The Office of Water Planning and Standards under Section 304 (a) of the Clean Water Act has begun development of a regulation based on health effects other than oncogenicity and environmental effects. Finally, the Office of Toxic Substances has completed a Phase I assessment of arsenic under the Toxic Substances Control Act.

Industrial Recognition of Hazard

Arsenic administered by either the intra-muscular or subcutaneous routes is rated as highly toxic in Sax, Dangerous Properties of Industrial Materials (22). Arsenic is also rated as highly toxic through ingestion, inhalation, and percutaneous routes in Patty, Industrial Hygiene and Toxicology.

A ten-fold reduction (to 0.005 mg/m^3) of the present OSHA standard for arsenic trioxide has been proposed (23).

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JB-07-05
JANUARY 19, 1981

HAZARDOUS WASTE LISTING BACKGROUND DOCUMENT

K085: Distillation or Fractionating Column Bottoms from the Production of Chlorobenzenes (T).

K105: Separated Aqueous Stream from the Reactor Product Washing Step in the Production of Chlorobenzenes (T).*/

Distillation or fractionation column bottoms from the production of chlorobenzenes,**/ and the separated aqueous waste stream from the reactor product washing step in the batch production of chlorobenzenes, are composed of a varying mixture of chlorobenzenes (dichlorobenzene through hexachlorobenzene) and benzyl chloride, and may also contain benzene and monochlorobenzene. The Administrator has determined that these waste streams are solid wastes and as solid wastes may pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, disposed of, transported or otherwise managed. Therefore, these wastes should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. Distillation or fractionating column bottoms from chlorobenzene production are likely to contain significant concentrations of dichlorobenzenes, trichlorobenzenes, tetrachlorobenzene, pentachloroben-

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*/In response to comment, we have revised this listing description to indicate that a wastewater stream may be generated from both batch and continuous processes. (See response to comment #4.)

**/Throughout this background document, the terms 'chlorobenzene(s)' and 'chlorinated benzene(s)' are used synonomously to denote the group of substituted benzene compounds in which one to six hydrogen atoms of benzene are replaced by chlorine atoms, with no ring substituents present other than chlorine or hydrogen.

zene and hexachlorobenzene. Benzyl chloride is expected to be present in significant concentrations. Benzene and monochlorobenzene may also be present in lesser concentrations depending on the efficiency of distillation . The dichlorobenzenes, trichlorobenzenes and tetrachlorobenzenes are all toxic. Pentachlorobenzene has been reported to induce cancers in some animal species. Hexachlorobenzene and benzene have been identified by EPA's Carcinogen Assessment Group (CAG) as having substantial evidence of carcinogenicity. Benzyl chloride is reportedly carcinogenic. Monochlorobenzene is toxic. All of the chlorobenzenes bioaccumulate.*/

2. The separated aqueous waste stream from the batch production of chlorobenzenes is believed to contain significant concentrations of benzene, several chloro benzenes, and 2,4,6-trichlorophenol, all of which present chronic toxicity hazards. Benzene and 2,4,6-trichlorophenol have been identified by CAG as having substantial evidence of carcinogenicity.

3. These waste constituents are capable of migration, mobility and environmental persistence if managed improperly, and have caused substantial hazard in actual damage incidents. Disposal of these distillation bottoms and the aqueous waste in uncontrolled landfills, therefore, could allow migration of contaminants to ground and surface waters and release of volatile toxicants to the air, while improper incineration may result in the generation of extremely hazardous compounds such as phosgene.

I. Industry Characterization and Manufacturing Process

A. Profile of the Industry

Twelve chlorinated benzene compounds can be formed during the chlorination of benzene including monochlorobenzene, three isomers of dichlorobenzene, three of trichlorobenzene, pentachlorobenzene and hexachlorobenzene; their structures and physical properties are illustrated in Figure 1 and Table 1. In 1979 chlorobenzene production totalled about 204,000 kkg, or about half of the available capacity (56). Most of the production is of mono-and dichlorobenzenes. Monochlorobenzene is the dominant commercial product; in 1978, production was approximately 134,000 kkg.(1) Production of ortho- and para-dichlorobenzene was estimated at 10,000 kkg each for that same year.(1) Production of 1,2,4-trichlorobenzene was 13,000 metric tons in 1973. It is estimated that approximately the same amount was produced in 1977.(1) Annual production of the commercially important tri- and tetrachlorobenzenes and of pentachlorobenzenes ranges from 1,000 - 50,000 kkg. Major producers of chlorobenzenes in the United States include: Allied Chemical Corporation (Syracuse, New York); Dow Chemical Company (Midland, Michigan); Monsanto Company (Sauget, Illinois); Montrose Chemical Corporation of California (Henderson, Nevada); PPG Industries, Inc. (Natrium, West Virginia); Specialty Organics, Inc. (Irwindale, California); and Standard Chlorine Chemical Company, Inc. (Delaware City, Delaware).(2) Certain companies, including the Olin Corporation, produce chlorobenzenes as intermediates rather than as end products. Distillation residues and aqueous waste streams from the chlorobenzene manufacturing phase of such processes are included in the present listing.

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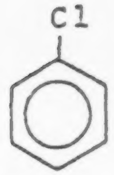
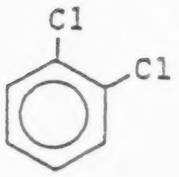
*/Certain of these wastes (particularly where the higher chlorinated benzenes are being produced) may contain polychlorinated biphenyls. (See Petition for Exemption under §6(e)(3)(b) of the Toxic Substances Control Act of Olin Corporation, dated June 28, 1979, noting concentrations of up to 8000 ppm PCB's in distillation residues from the production of pentachlorobenzene). The Agency is not presently listing PCB's as a waste constituent of concern pending integration of the RCRA Subtitle C and TSCA PCB regulations. The regulated community and permit writers should be aware, however, of the possibility of hazardous levels of PCB's in these wastes.

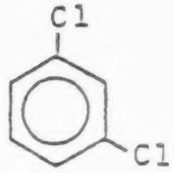
Figure 1. Chemical Structures of the Chlorinated Benzenes



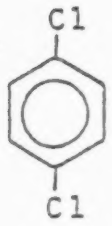
Monochlorobenzene



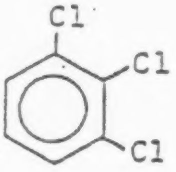
1,2-Dichlorobenzene
o-Dichlorobenzene



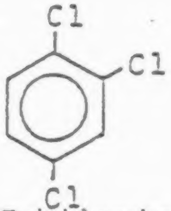
1,3-Dichlorobenzene
m-Dichlorobenzene



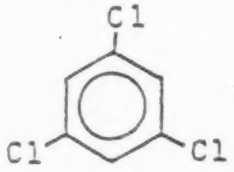
1,4-Dichlorobenzene
p-Dichlorobenzene



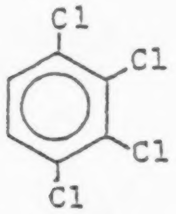
1,2,3-Trichlorobenzene



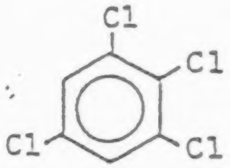
1,2,4-Trichlorobenzene



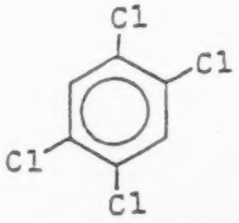
1,3,5-Trichlorobenzene



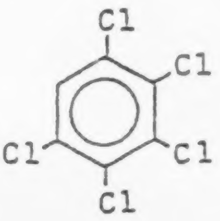
1,2,3,4-Tetrachlorobenzene



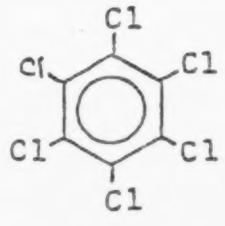
1,2,3,5-Tetrachlorobenzene



1,2,4,5-Tetrachlorobenzene



Pentachlorobenzene



Hexachlorobenzene

TABLE 1. PHYSICAL PROPERTIES OF CHLORINATED BENZENES[a]

Compound Name	CAS No.	Empirical formula	Mol. Wt.	M.p., °C	B.p.[b] °C	Vapor Press.	Density[c]	Water Solubility (mg/L)[d]	Log P_{oct}
Monochlorobenzene	108-90-7	C_6H_5Cl	112.56	-45.6°	132°	10mm/22°	1.1058	500[e]	2.84[f]
1,2-Dichlorobenzene	95-50-1	$C_6H_4Cl_2$	147.01	-17.0°	180.5°	1mm/20°	1.3048	140[e]	3.38[f]
1,3-Dichlorobenzene	541-73-1	$C_6H_4Cl_2$	147.01	-24.7°	173°	1mm/12°	1.2884	123[e]	3.38[f]
1,4-Dichlorobenzene	106-46-7	$C_6H_4Cl_2$	147.01	53.1°	174°	0.4mm/25°	1.2475	79[e]	3.39[f]
1,2,3-Trichlorobenzene	87-61-6	$C_6H_3Cl_3$	181.45	54°	219°	1mm/40°			4.1[g,h]
1,2,4-Trichlorobenzene	120-82-1	$C_6H_3Cl_3$	181.45	17°	213.5°	1mm/38°	1.4542	30[i]	
1,3,5-Trichlorobenzene	108-70-3	$C_6H_3Cl_3$	181.45	64°	208°[j]	10mm/78°			
1,2,3,4-Tetrachlorobenzene	634-66-2	$C_6H_2Cl_4$	215.90	47.5°	254°	1mm/68°		0.36[e]	
1,2,3,5-Tetrachlorobenzene	634-90-2	$C_6H_2Cl_4$	215.90	54.5°	246°	1mm/58°			
1,2,4,5-Tetrachlorobenzene	95-94-3	$C_6H_2Cl_4$	215.90	140.5°	246°	40mm/146°	1.858(22°)		
Pentachlorobenzene	608-93-5	C_6HCl_5	250.34	86°	277°	1mm/99°	1.8342(16°)		
Hexachlorobenzene[k]	118-74-1	C_6Cl_6	284.79	230°	322°	1mm/114°	1.5691(24°)	0.020[i]	5.8[g]

(a) From Ref. 56; Data are from standard reference sources, except partition coefficient and solubility data, for which references are cited. (b) At 1 atm. (c) At 20C except as noted. (d) At 25C. (e) Ref. 11. (f) Ref. 20. (g) Ref. 22. (h) isomer unspecified. (i) Ref. 28. (j) At 763 mm. (k) Ref. 51.

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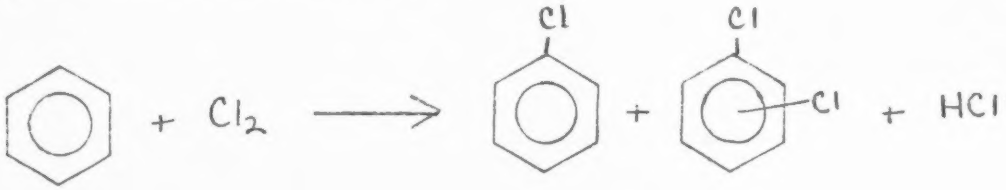
B. Manufacturing Process

Chlorobenzene, dichlorobenzenes, and higher chlorinated benzenes are produced in batch and in continuous processes by chlorination of benzene in the presence of a Friedel Crafts catalyst, such as ferric chloride, as shown in the following reaction*/for monochlorobenzene:



Because higher chlorinated benzenes always result from the direct chlorination of benzene, chlorobenzene production is a multiple product operation, i.e. a range of chlorinated benzenes may be produced. Product ratios are influenced by temperature, mole ratios of the feedstocks, residence time, and catalyst. The crude reaction product of a continuous process may be recycled to the process to achieve the desired final product mixture. Depending on the final product mixture, chlorobenzenes are purified by fractional distillation and/or crystallization. Continuous chlorination processes, in contrast to batch processes, minimize the amount of higher chlorinated products, thereby maximizing monochlorobenzene yields.

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*/ 1,3-Dichlorobenzene, 1,3,5-trichlorobenzene and 1,2,3,5-tetrachlorobenzene are not produced by the method discussed below.

1. Production of Monochlorobenzene

a) Continuous Process (modified from references 1,6, and 7)

As shown in Figure 2, in a typical continuous process for the production of chlorobenzenes, anhydrous benzene and chlorine are introduced into a reactor operating at a bottom temperature of 90-125°C and a top temperature of about 80°C. Benzene is introduced near the top of the column, and an equimolar amount of chlorine is introduced near the midpoint of the reactor. A variety of catalysts may be used, usually iron or ferric chloride impregnated on a suitable carrier.

The overhead reactor effluent consisting of hydrogen chloride and benzene passes through a condenser which condenses the benzene for recycle. Hydrogen chloride is recovered by passing the uncondensed gas through a scrubber tower containing a chlorination catalyst, thereby removing unreacted chlorine. The mixture is then passed through one or more towers in which chlorobenzenes are used to remove organic contaminants. The resultant hydrogen chloride is then recovered as either an anhydrous product or as a 30-40% aqueous solution. (If the hydrogen chloride must meet a low organic specification, a carbon column may be used prior to or after the water absorption tower.)

The bottom effluent from the reactor comprises an equilibrium mixture of benzene and mixed chlorobenzenes. To maximize monochlorobenzene production, a high recycle rate of benzene is maintained (20:1). Chlorobenzene is withdrawn at

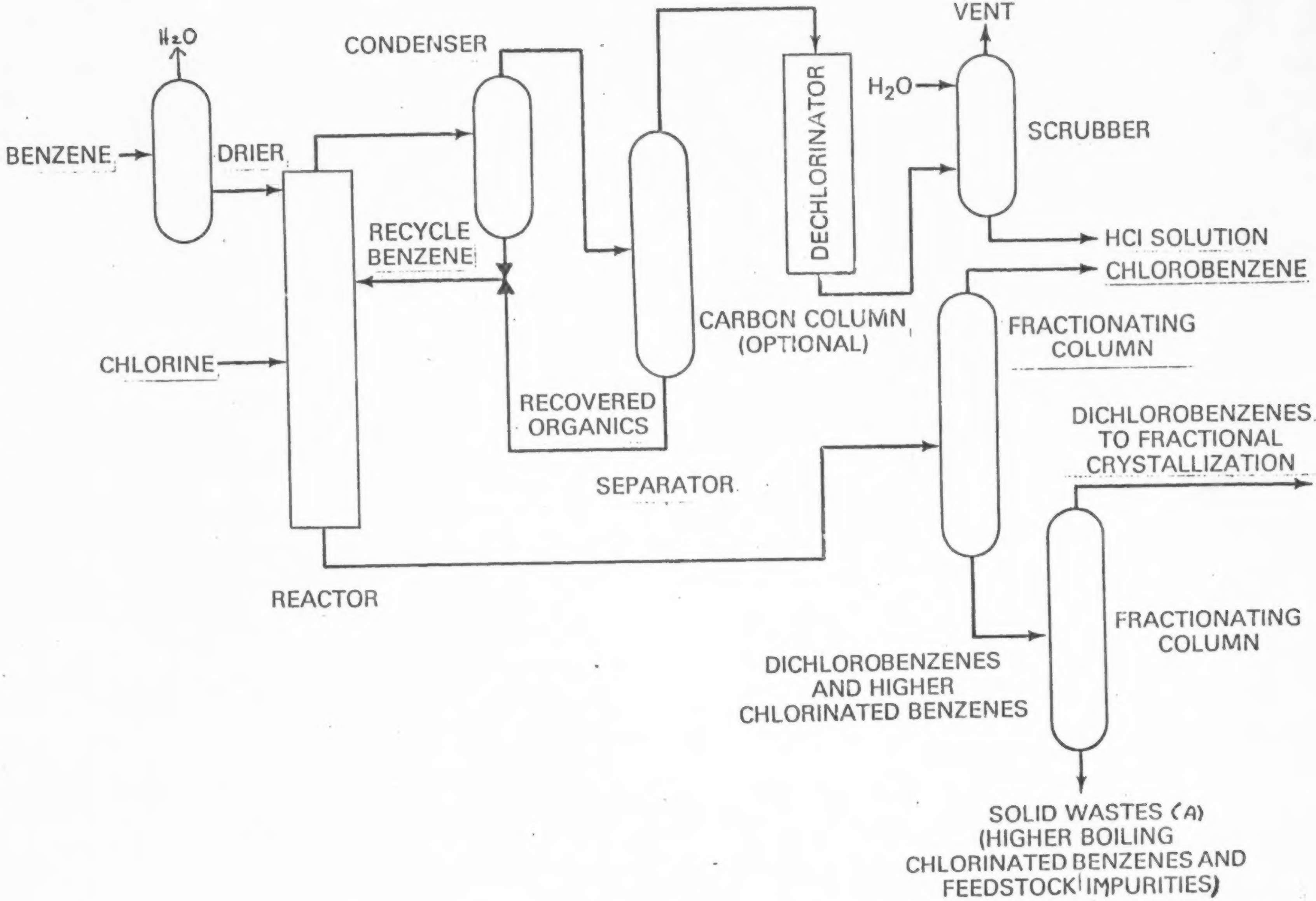
H₂O
BENZENE
DRIER
CONDENSER
RECYCLE BENZENE
CHLORINE
REACTOR
RECOVERED ORGANICS
SEPARATOR
CARBON COLUMN (OPTIONAL)
DECHLORINATOR
H₂O
VENT
SCRUBBER
HCl SOLUTION
CHLOROBENZENE
FRACTIONATING COLUMN
DICHLOROBENZENES TO FRACTIONAL CRYSTALLIZATION
DICHLOROBENZENES AND HIGHER CHLORINATED BENZENES
FRACTIONATING COLUMN
SOLID WASTES (A) (HIGHER BOILING CHLORINATED BENZENES AND FEEDSTOCK IMPURITIES)

FIGURE 2
CONTINUOUS PRODUCTION OF CHLOROBENZENE (MODIFIED FROM 7)

a rate equal to that at which benzene is fed and chlorinated, and flows to a fractionating column which operates at a bottom temperature of aproximately 190°C and top temperature of 140°C. The higher boiling bottom products (mostly dichlorobenzenes) are continuously bled at approximately 2% of the product feed to a fractionating column for recovery of the di- and trichlorobenzenes. The wastes of concern (waste A in Figure 2) are the bottoms from the two fractionating columns.*/

b) Batch Process

Chlorobenzenes may also be manufactured by a batch process as shown in Figure 3. Dry benzene is charged into an agitated glass-lined or iron (steel) reactor. Either iron turnings or anhydrous ferric chloride are used as a catalyst and remain in the chlorinator after each product batch is withdrawn. The desired product mix is achieved by adjustment of chlorine concentration and reactor temperature. If monochlorobenzene is the desired product, about 60 percent of the stoichiometeric requirement of chlorine is used, and the reaction temperature is maintained in the range of 20° to 30°C for 10 to 16 hours. If poly-substituted chlorobenzenes (generally dichlorobenzenes) are desired in addition to monochlorobenzene, the reaction is run at a temperature of 55° to 60°C for approximately six hours.

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*/ In some processes, the further fractionating steps for recovery of higher chlorobenzenes is not employed, in which case the waste of concern is the column bottoms from the first fractionating column.

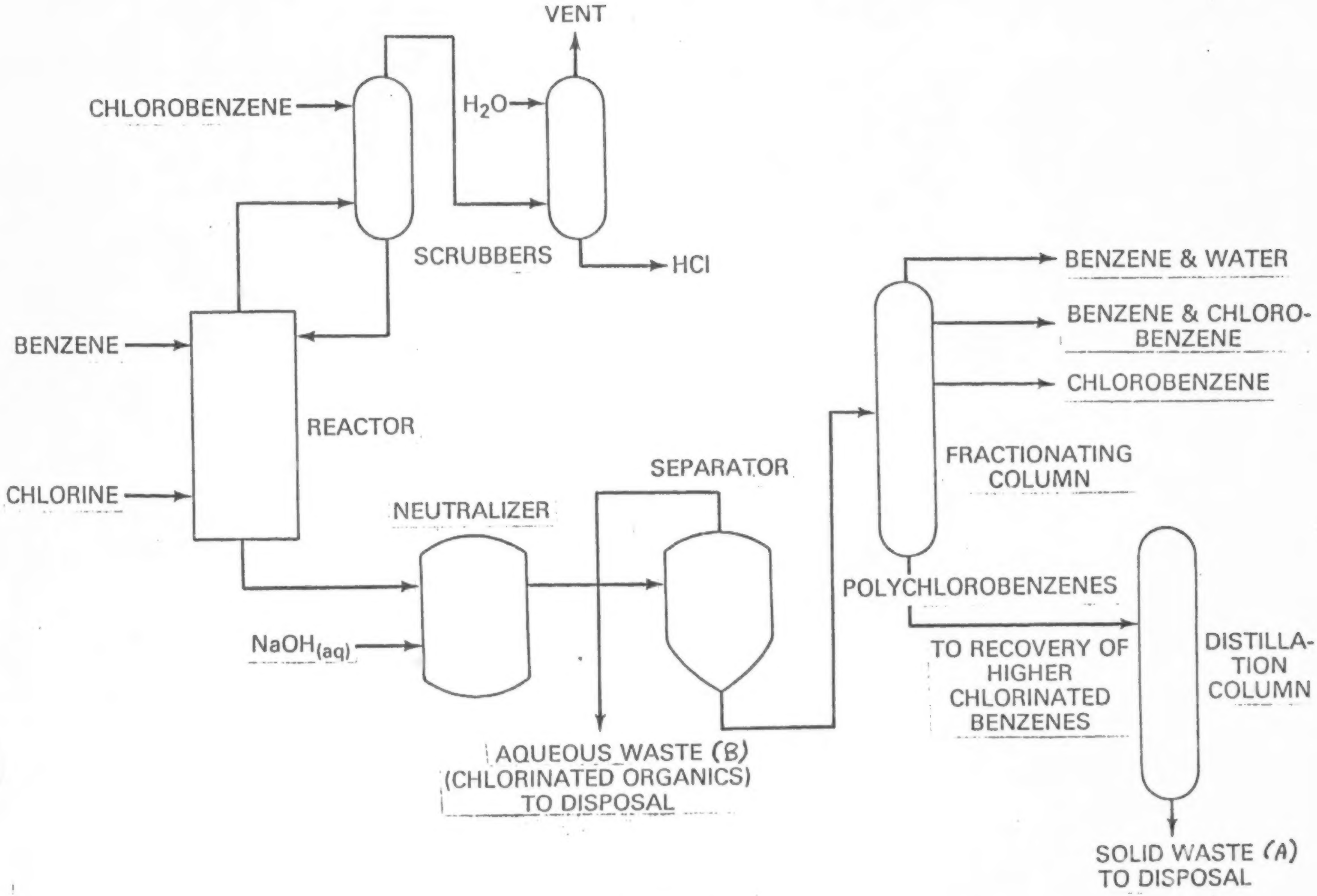
VENT
CHLOROBENZENE
H_2O
SCRUBBERS
HCl
BENZENE
CHLORINE
REACTOR
NEUTRALIZER
$NaOH_{(aq)}$
SEPARATOR
AQUEOUS WASTE (B)
(CHLORINATED ORGANICS)
TO DISPOSAL
BENZENE & WATER
BENZENE & CHLOROBENZENE
CHLOROBENZENE
FRACTIONATING COLUMN
POLYCHLOROBENZENES
TO RECOVERY OF HIGHER CHLORINATED BENZENES
DISTILLATION COLUMN
SOLID WASTE (A)
TO DISPOSAL

FIGURE 3
BATCH PRODUCTION OF CHLOROBENZENES (MODIFIED FROM 6)

Hydrogen chloride is recovered in a manner similar to that of continuous processes by scrubbing with chlorobenzene to remove organic contaminants and absorbing the product gas in water to give hydrochloric acid. The chlorobenzene product is washed in an agitated reactor with an aqueous solution of sodium hydroxide (10 percent by weight). The separated aqueous layer (waste B in Figure 3) is a separate waste, and is the second waste included in this listing.*/

After the neutralized organic layer is separated, it is sent to a fractionation column for product separation. As is the case in the continuous chlorination process, waste A (distillation or fractionation column bottoms are also generated). Table 2 illustrates the estimated product distribution for a fully chlorinated batch for which 100 percent of the theoretical amount of the chlorine requirement for monochlorobenzene was consumed.(6)

TABLE 2

PRODUCT DISTRIBUTION OF A CHLOROBENZENE BATCH REACTION (6)

Distillate Fraction	Component	% by weight
1	Benzene and water	3
2	Benzene and chlorobenzene	10
3	Chlorobenzene	75
4	Chlorobenzene and dichlorobenzene	10
5	Tar (trichlorobenzene and higher)	2

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*/This aqueous stream is not expected to be present in most continuous processes, since during the stripping step in the continuous process (see Fig. 2) the temperature at the bottom of the condenser column is such that residual hydrogen chloride and benzene are removed, making a product washing step unnecessary. However, comments indicated that an aqueous waste stream is generated from at least one continuous manufacturing process. We therefore have revised the listing description of this waste to indicate that it is hazardous irrespective of the type of manufacturing process.

Most batch processes include further distillation steps to to separate higher chlorinated benzenes, particularly o- and p-dichlorobenzene and trichlorobenzene.*/ The chlorobenzene and dichlorobenzene fraction (No. 4) is usually further distilled to recover p-dichlorobenzene and o-dichlorobenzene. Trichlorobenzene may also be recovered. The tarry residue (Table 2, Fraction 5, waste A in Figures 2 and 3, the solid waste of concern) consists chiefly of trichloro- and higher chlorinated benzenes.

2. Production of Polychlorobenzenes

As noted previously, aromatic chlorination is a multiple product process; most polychlorobenzenes can be produced *via* processes similar to those described above. Reaction conditions are, however, likely to be somewhat different. Higher reaction temperatures, longer reaction times and higher chlorine to benzene ratios are likely modifications. A process configuration for production of dichlorobenzenes is shown in Figure 4.

Dichlorobenzenes(56)

o-Dichlorobenzene and *p*-dichlorobenzene are produced by chlorinating benzene or monochlorobenzene at 150°C-190°C over a ferric chloride ($FeCl_3$) catalyst. An orienting catalyst such as benzensulfonic acid or *p*-dichlorobenzene may also be employed. The isomers can be separated by fractional distillation, or by crystallizing the p-dichlorobenzene. Another method of obtaining the para isomer is by chlorination of crude dichloro-

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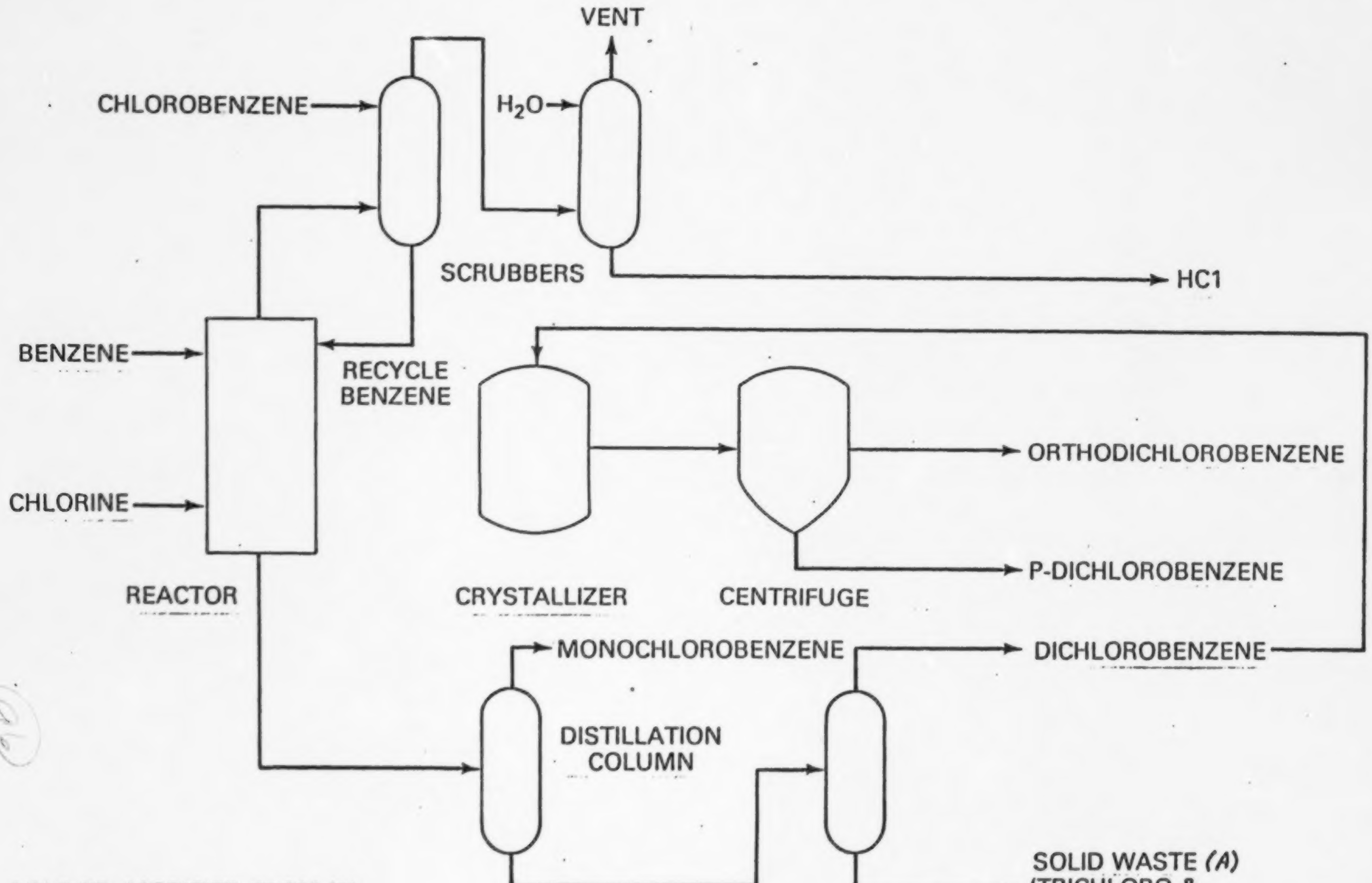
*/Table 2 is a product mix prior to this second distillation


VENT
CHLOROBENZENE
H_2O
SCRUBBERS
HC1
BENZENE
RECYCLE BENZENE
CHLORINE
REACTOR
CRYSTALLIZER
CENTRIFUGE
ORTHODICHLOROBENZENE
P-DICHLOROBENZENE
MONOCHLOROBENZENE
DICHLOROBENZENE
DISTILLATION COLUMN
SOLID WASTE *(A)*
(TRICHLORO &
HEAVIER)

SOURCE: MODIFIED FROM (8)

FIGURE 4
PRODUCTION OF HIGHER CHLOROBENZENES

benzene over $FeCl_3$, whereby the more reactive ortho isomer is converted to 1,2,4-trichlorobenzene. *p*-Dichlorobenzene can then be separated by distillation. The purified grade of *o*-dichlorobenzene is obtained by efficient redistillation of the technical product. m-Dichlorobenzene can be prepared by isomerization of o-dichlorobenzene and *p*-dichlorobenzene with heat under pressure in the presence of a catalyst.

Trichlorobenzenes.(56)

1,2,4-Trichlorobenzene is produced along with 1,2,3-trichlorobenzene by chlorination of *o*-dichlorobenzene at 25 to 30 °C in the presence of ferric chloride, then separated from the 1,2,3-trichlorobenzene by distillation. 1,3,5-Trichlorobenzene can be produced readily only by special methods such as by the diazotization of 2,4,6-trichloroaniline followed by treatment with alcohol. Additional methods of synthesis for trichlorobenzenes are reviewed in the report by Ware and West.(57)

Tetrachlorobenzenes.(56,57)

1,2,3,4-Tetrachlorobenzene can be produced by chlorinating 1,2,3-trichlorobenzene in the presence of a catalyst. 1,2,4,5-Tetrachlorobenzene is manufactured by chlorination of 1,2,4-trichlorobenzene over aluminum amalgam. To produce 1,2,3,5-tetrachlorobenzene, 1,3,5-trichlorobenzene can be chlorinated over aluminum amalgam. In practice, 1,2,3,4- and 1,2,3,5-tetrachlorobenzene are produced only as by-products in the manufacture of 1,2,4,5-tetrachlorobenzene.

Pentachlorobenzene and Hexachlorobenzene (8,9)

Pentachlorobenzenes is formed by the chlorination of benzene in the presence of ferric or aluminum chloride at temperatures of 150 to 200°C, or by the chlorination of any of the lower chlorobenzenes. It may also be formed in small amounts when trichloroethylene is heated to 700°C(56).

Hexachlorobenzene is reported not to be produced commercially *via* catalytic (ferric chloride) chlorination of benzene. When generated as a by-product of the processes described in this document, it is found in the fractionating column bottoms.

C. Commercial Uses of Chlorobenzenes(56)

Most (50-70%) monochlorobenzene is used as a chemical intermediate in the synthesis of chloronitrobenzenes, herbicides, diphenyloxide, and silicones. The remainder is used as a solvent for herbicides, for synthetic processes and for degreasing operations.

Sixty-five percent of the *o*-dichlorobenzene produced is used in organic synthesis, primarily as a pesticide intermediate. Fifteen percent is used as a solvent in the production of toluene diisocyanate. Miscellaneous solvent uses, such as for oxides of nonferrous metals, for soft carbon deposits, for tars and wool oils in the textile industry, and for degreasing leather and automobile and aircraft engine parts, account for most of the rest of the annual production of *o*-dichlorobenzene. It is also a solvent in formulated toilet bowl cleaners and drain cleaners. Other uses in metal polishes, in industrial odor control, as a heat transfer fluid, and in rustproofing mixtures account for 4 percent of annual *o*-dichlorobenzene production. *o*-Dichlorobenzene is registered as a fumigant and insecticide against termites, beetles, bacteria, slime, and fungi.

Eighty percent of the annual production of *p*-dichlorobenzene goes to home and industrial use: as a moth control agent (30 percent) and as a space odorant (50 percent), especially in toilets and rest rooms.

Miscellaneous uses as a dye intermediate, insecticide, extreme pressure lubricant, forming agent for grinding wheels, disintegrating paste for molding concrete and stoneware, and as an intermediate in the manufacture of 2,5-dichloroaniline and polyphenylenesulfide resins account for the remaining 10-20% of the consumption of *p*-dichlorobenzene. No uses were identified for *m*-dichlorobenzene apart from its conversion to higher chlorobenzenes.

The most widely used isomer of tetrachlorobenzene is 1,2,4,5-tetrachlorobenzene, which is used primarily as an intermediate in chemical synthesis. Of the approximately 8,000 kkg consumed in 1973, 2,700 kkg were used to produce the fungicide and bactericide 2,4,5-trichlorophenol, 4,500 kkg were used in the production of the herbicide 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), and the remainder went to miscellaneous uses. 1,2,4,5-Tetrachlorobenzene may also be used as an impregnant for moisture resistance, as electrical insulation and as temporary packing protection. According to a recent review, 1,2,4,5-tetrachlorobenzene is now used exclusively to make 2,4,5-T and its esters, however, it is a component of the transformer fluid, Iralec©. Thus, the use pattern for this material appears to be in flux. EPA has no information on uses of 1,2,3,4- and 1,2,3,5-tetrachlorobenzenes except that the former, as a mixture with the 1,2,4,5-isomer, is an intermediate in the synthesis of the fungicide pentachloronitrobenzene.

II. Waste Composition and Management

1. Fractionation Bottoms

The distillation or fractionation bottoms from the production of monochlorobenzene consist primarily of the higher polychlorinated benzenes (trichlorobenzenes and higher), benzyl chloride and chlorotoluenes*/ resulting from the chlorination of toluene impurities in benzene feedstock, and lesser concentrations of feedstock benzene, product chlorobenzene, and dichlorobenzenes (depending on the efficiency of the fractionating step). The relative concentrations of the various chlorobenzenes in these wastes vary according to reaction conditions and the efficiency of fractionation. In general, when monochlorobenzene is the favored by-product, dichlorobenzene will probably be the most prevalent of the chlorinated benzenes in the distillation residue (and in the waste if there is no subsequent distillation step to recover dichlorobenzenes as product) since benzene is being chlorinated for less time, so that smaller concentrations of tetra- to hexachlorobenzene are formed. If dichlorobenzenes are recovered as product, trichlorobenzenes represent the largest fraction in the waste. When the reaction is pushed in the direction of polychlorinated benzenes, there will be more trichloro through hexachlorobenzene in the waste stream.

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*/ Both o- and p-chlorotoluene are expected to be present. These constituents are not considered to be of regulatory concern because of their low chronic toxicity. Further information as to the validity of this conclusion is solicited, however.

Waste composition, and especially the concentrations of the various chlorinated benzenes, also will vary quantitatively, although not qualitatively, depending on whether a continuous or batch production process is used. Batch processes would tend to have somewhat higher concentrations of higher chlorinated benzenes, since benzene chlorination occurs for a longer period.

Table 2 gives an estimate of wastes resulting from a batch reaction favoring monochlorobenzene production. Distillation tars (Fraction 5), consisting principally of trichlorobenzenes and isomers of higher degree of chlorination are estimated to comprise roughly 2% by weight of the total reaction products.

Table 3 gives a second estimate of waste composition from a batch process favoring monochlorobenzene. Small amounts of unreacted benzene, hydrogen chloride and chlorobenzenes are vented to the atmosphere; small concentrations of these constituents are expected to remain in the distillation bottoms. The distillation residues (Table 3, Fraction 6), the first-listed waste of concern in this document, comprise about 80% of the wastes generated in this process.

Table 3(2)

ESTIMATED LOSS OF MATERIALS DURING CHLOROBENZENE MANUFACTURE
(BATCH PROCESS)

FRACTION	COMPOUND	SOURCE	QUANTITY (kg/kkg monochlorobenzene)
1	Hydrogen chloride	Hot scrubber vent	1.4
2	Monochlorobenzene	o-Dichlorobenzene column	.88
3	Dichlorobenzenes (isomers not specified)	do	3.7
4	Monochlorobenzene	Fractionating towers	4.0
5	Dichlorobenzenes	"	0.1
6	Polychlorinated benzenes	Distillation residues*	44.0

*waste A, Figures 2 and 3

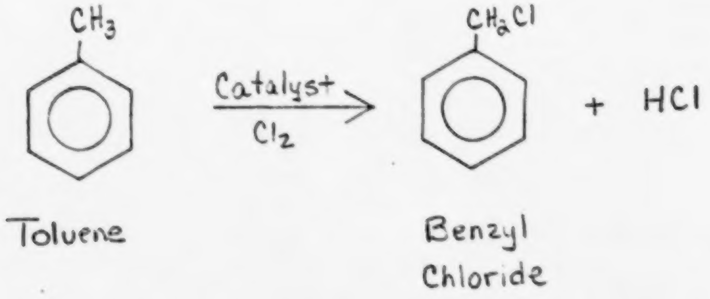
A third reference(3) (shown in Table 4) taken from the patent literature, and involving a continuous process, shows monochlorobenzene present in fairly substantial concentrations in the solid waste; the estimate for the production of heavier chlorinated benzenes (31 kg/kkg of monochlorobenzene produced) does not differ greatly from the estimate given in Table 2.

TABLE 4

ESTIMATED EMISSIONS FROM CHLOROBENZENE MANUFACTURE: Chlorination of Benzene, Continuous Process(3)

	Emission (kg/kkg)
Species	Solid
Benzene	trace
Monochlorobenzene	2.6
Polychlorinated benzenes	31
	33.6

The solid wastes (from both continuous and batch processes) are also expected to contain significant concentrations of benzyl chloride and o- and p-chlorotoluene resulting from chlorination of toluene impurities in benzene feedstock.*/ (As noted above, the chlorinated toluenes are not waste constituents of concern). The specific reaction pathways for these constituents are given below:



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*/ Toluene is believed to be the most significant feedstock impurity. Benzene may typically contain up to 1% toluene(9)

The above side reactions are believed to be those most likely to occur under the usual conditions of benzene chlorination. Virtually all of these substances are expected to be present in the distillation bottoms since they are high boiling chemicals that the distillation process is designed to eliminate.

2. Separated Aqueous Stream from the Reactor Product Washing Step (batch process)

The aqueous stream from the reactor product washing step in the production of chlorinated benzenes will contain benzene, and all of the chlorinated benzenes in solution (along with water and caustic soda used in the washing operation). The concentrations of these constituents in the waste will depend on their concentration in the reaction product stream and their solubilities in the alkaline wash solution. While the Agency does not presently have precise information on these compounds' solubilities in basic solutions, they are not believed to differ significantly from their solubilities in water (if anything, solubilities would be slightly higher in basic solutions). Thus, the most soluble component, benzene (water solubility up to 1,780 ppm), would probably be the principal waste constituent, and monochlorobenzene and o- and p-dichlorobenzene would also be present in fairly significant levels (water solubilities from 79 ppm to 500 ppm, respectively)(See Table 1) would also be present in significant concentrations. The remaining chlorinated benzenes are probably present at much lower levels, since their solubilities (See Table 1) are quite low. Phenols could also be formed if temperatures are sufficiently high to create hydrolysis conditions, and a highly alkaline wash mixture is used.(58) Chlorinated phenols could also be present from the phenolization of the di- and tri-chlorobenzenes, although concentrations of phenols and chlorinated phenols would probably be small.

Table 5 below shows organic contaminants found in the wastewater stream from chlorobenzene manufacture at a Dow plant.

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TABLE 5

PRIORITY POLLUTANTS IDENTIFIED IN AQUEOUS WASTESTREAM FROM PRODUCT WASHING STEP IN PRODUCTION OF CHLOROBENZENES(29)

	Concentration mg/l		Loading kg/day
	sampling a	sampling b	(based on sampling a)
------------	------------	------------	------------
------------	------------	------------	------------
------------	------------	------------	------------
------------	------------	------------	------------
------------	------------	------------	------------
------------	------------	------------	------------
------------	------------	------------	------------
------------	------------	------------	------------
------------	------------	------------	------------
------------	------------	------------	------------

*The underlined data are those obtained from proprietary reports and data files.

3. Waste Management

Waste management practices for the distillation residues generally involve disposal in on-site and off-site landfills (1). Incineration is also practiced (2).

The separated aqueous stream generally is sent to wastewater treatment.(1) The most feasible treatment method is activated carbon preceded by sand filtration.(1) A wastewater treatment sludge is generated which is assumed to be hazardous unless generators show otherwise. (See §261.3(a)(2)(ii).)

III. Hazards Posed by the Waste

As noted above, the distillation wastes are expected to contain significant concentrations of tri- through hexachlorobenzene, and benzyl chloride, lesser concentrations of dichlorobenzenes, and some monochlorobenzene and benzene. Hexachlorobenzene and benzene have been identified by EPA's Carcinogen Assessment Group as having substantial evidence of carcinogenicity. Pentachlorobenzene is reported to induce cancers in some animal species. All the chlorobenzenes are toxic to the liver, kidney and central nervous system, in varying degree.(56) Benzyl chloride is reportedly carcinogenic. The remaining constituents present acute and chronic toxicity hazards. All are priority pollutants. In addition, all of the chlorinated benzenes are bioaccumulative (based on extremely high octanol/water partition coefficients), and so could pose an additional hazard even if exposure is only to small concentrations of the pollutant.

The aqueous waste stream contains benzene, chlorobenzenes through trichlorobenzene, and (under certain conditions) high chlorinated phenols (See Table 5). 2,4,6-Trichlorophenol has been identified by the Carcinogen Assessment Group as having substantial evidence of carcinogenicity. In addition, it presents other chronic toxicity hazards, and is also mutagenic.

In light of the reported concentrations of these hazardous constituents, these waste streams are clearly of regulatory concern. Indeed, for the carcinogens in the wastes, there is no known safe level of exposure, every exposure likely giving rise to at least one cancer in a portion of the population, regardless of exposure concentration.(10) The Agency thus requires strong assurance that these waste constituents are incapable of migration, mobility, and persistence in the event of improper management to justify not listing this class of wastes. Such assurance does not appear possible.

All of the waste constituents have proved capable of migration, of mobility through soils, and of environmental persistence in the course of actual waste management practice, creating a substantial potential for hazard. Benzene and all of the chlorinated benzenes through pentachlorobenzene have been detected in air, basement sump and solid surface samples collected in the vicinity of the Love Canal waste disposal site in Niagara, New York.(5) Benzyl chloride has been identified as leaching from Hooker's Hyde Park site in Niagara, New York,(12) and has been shown to persist in the atmosphere in the New Jersey area for considerable periods of time.(15)

Hexachlorobenzene has likewise been shown to migrate *via* air and groundwater pathways and to persist following migration. One damage incident involving hexachlorobenzene occured in Louisiana in the early 1970s. Inhalation exposure to hexachlorobenzene resulted from transport of hexachlorobenzene-contaminated wastes, resulting in dangerously elevated hexachlorobenzene concentrations in humans and animals along the route.(12) Hexachlorobenzene has also been detected in concentrations exceeding background levels in many groundwater monitoring samples taken at various locations at a chemical company dump. (Table 7.2. reference 1)

The higher chlorinated phenols present in the wastewater stream also are capable of migration, mobility, and persistence. Although they are subject to biodegradation (*id.*) by specifically adapted organisms, these compounds could persist for long periods of time in the abiotic conditions characteristic of most aquifers.(80) Migratory potential is thus substantial, and thus, if migration occurs, chlorinated phenols are mobile and persistent. For example, in a damage incident at Montebello, California, involving wastes from 2,4 dichlorophenol manufacture, 2,4-dichlorophenol and other phenolic compounds proved capable of passing through soils and causing longterm pollution of groundwater. Contamination of groundwater by 2,4-dichlorophenol and other hazardous compounds has also been reported in East St. Louis, Ill. The source of the compounds was the Monsanto chemical dump.(12)

Since all of the waste constituents of concern have proven capable of migration, mobility, and environmental persistence, and have in fact caused substantial hazard in acutual waste management practice, the Agency believes that the waste constituents could migrate and reach environmental receptors if the wastes are improperly managed. Landfilling the waste without adequate cover could easily result in volatilization of hexachlorobenzene and benzene. Solubilization of hazardous compounds could occur if rainwater is allowed to percolate through the waste or run off the surface of exposed waste. Waste constituents could then be released if landfills are improperly designed (built without leachate control in areas with permeable soil or located in areas where soils have low attenuative capacity), or managed. Improperly designed wastewater treatment ponds pose the same risk. In the case of improperly managed landfills, surface run-off might also transport compounds that have adsorbed to suspended particulates. Contaminant-bearing leachate and surface run-off may eventually enter ground and surface waters, polluting valuable water supplies and adversely affecting aquatic organisms.

Improper incineration of the distillation residues provides another means by which toxic compounds can be generated and introduced into the environment. If incineration is inadequate (for instance, if temperatures are insufficient or residence time incomplete), inadequate combustion can result in the formation of substances (such as phosgene) that are even more toxic than the original waste.(1) These contaminants can be emitted from the incinerator to the atmosphere and dispersed in the environment.

IV. Health and Ecological Effects

Health and ecological effects and potential transport mechanisms for the constituents of concern that might be found in the distillation bottoms and the separated aquaeous waste stream from manufacture of chlorobenzenes are described below:

Benzene

Health Effects Benzene is a human carcinogen. Exposure to benzene as a result of inhalation induces abnormalities in the blood and causes leukemia.(31-33) Benzene administered subcutaneously has been teratogenic in mice at extremely low doses [3 ml/kg].(34) Chronic inhalation of this chemical in low doses by rats has caused both inhibition and resorption of embryos.(35) Benzene is also mutagenic when administered orally to mice at extremely low doses [1 mg/kg].(36)

Exposure of humans to benzene has resulted in the reduction of blood cells, aplastic anemia, impairment of the immunologic system, and a variety of mutagenic effects in lymphocytes and bone marrow.(37-42) Oral ingestion of benzene in small amounts (50 mg/kg), or one-seventieth of the oral LD_{50} in rats, has proven lethal to humans.(43)

Regulatory Recognition of Hazard - OSHA has set a PEL for benzene at 10 ppm with a ceiling level of 30 ppm for 10 minutes. EPA's Office of Air Quality Planning and Standards and Toxic Substances are performing a pre-regulatory assessment of benzene based on its production volume, spill reports and health and environmental effects. Additionally, EPA's CAG has determined that there is substantial evidence that benzene is a carcinogen. EPA has estimated 0.66 ug/l as the concentration in ambient water which could result in a 10^{-6} additional risk for cancer from the consumption of contaminated drinking water and contaminated aquatic organisms (65). The Consumer Product Safety Commission requires benzene to carry special labelling.

Benzene is a priority pollutant in accordance with §307 of the Clean Water Act of 1977 and is listed as a hazardous waste or hazardous waste constituent in final or proposed regulations of California, Maine, New Mexico and Oklahoma.

Industrial Recognition of Hazard - Benzene is designated as highly toxic in industrial handbooks, and represents a fire and moderate exposure hazard.

Additional information on the health and ecological effects of benzene may be found in Appendix A.

Chlorobenzenes:(13) Chlorobenzenes have moderate acute toxicity but, because they bioaccumulate to a significant degree, chlorobenzenes may pose a substantial hazard if chronic exposure occurs. They are relatively mobile in the environment and likely to persist for long periods of time because biodegradation is slow.

Chlorobenzene (monochlorobenzene, MCB)

Health effects - Monochlorobenzene is a central nervous system depressant, with the typical anesthetic effect produced by most chlorinated benzenes (45,46); degeneration of the liver and kidney may develop on chronic exposure. Depending on dosage, acute inhalation produces narcosis, neuropathy and death.(46) The metabolism of monochlorobenzene may lead to the formation of carcinogenic active intermediates.(48) The weighted average bioconcentration factor for mono-chlorobenzene is calculated to be 10.3.(13)

Regulatory Recognition of Hazard - The OSHA PEL for chlorobenzene is a TWA of 75 ppm. EPA's Office of Water and Waste Management provides technical assistance data and regulation for chlorobenzene under Section 311 of the Clean Water Act. They are also involved with pre-regulatory assessment under the Safe Drinking Water Act. The Office of Air, Radiation and Noise and the Office of Research and Development are involved with preregulatory assessment under the Clean Air Act. The Office of Toxic Substances has developed test rule recommendations under Section 4(e) of the Toxic Substances Control Act.(56)

Monochlorobenzene is listed as a priority pollutant in accordance with §307 of the Clean Water Act of 1977, and final or proposed regulations of Maine, New Mexico, Oklahoma and California list chlorobenzene as a hazardous waste or a component of hazardous waste.

Additional information on the health and ecological effects of monochlorobenzene may be found in Appendix A.

Dichlorobenzenes: The bioconcentration factors for three dichlorobenzenes range from 60-89.(13) Their bioaccumulative properties are therefore moderate.

o-Dichlorobenzene

Health Effects - O-dichlorobenzene is very toxic in rats [oral LD_{50} = 500 mg/Kg].(49) Human death has also occurred at this level.(43) Chronic occupational exposure to this chemical and its isomer is toxic to the liver, central nervous system and respiratory system.(13) Chronic feeding of ortho-dichlorobenzene to rats in small doses causes anemia as well as liver damage and central nervous system depression.(52)

Regulatory Recognition of Hazard - o-dichlorobenzene has been designated as a priority pollutant under Section 307(a) of the CWA. The OSHA PEL for o-dichlorobenzene is 50 ppm for an 8-hour TWA. o-Dichlorobenzene was selected by NCI for Carcinogenesis Bioassay, September 1978, and is listed as a hazardous waste, or a component thereof, in final or proposed regulations of the States of California, New Mexico and Oklahoma. The U.S. EPA ambient water quality criterion for dichlorobenzenes (all isomers) is 400 ug/l. (13,65). U.S. EPA has also established criteria for freshwater and marine aquatic life.

p-Dichlorobenzene

Health Effects - p-dichlorobenzene is toxic in rats (oral LD_{50} = 500 mg/kg](53)), and is lethal to humans ingesting similar amounts. (43) At smaller dose levels (300 mg/kg) adverse effects are noted on liver and kidney.(43) This chemical has induced growth depression, liver cell necrosis and death in animals exposed by inhalation.(56)

Regulatory Recognition of Hazard - p-dichlorobenzene has been designated as a priority pollutant under Section 307(a) of the CWA. The OSHA PEL standard is 75 ppm (TWA). It is listed as a hazardous waste or a component thereof in final or proposed regulations of the states of California, New Mexico, and Oklahoma. Additional information on the health and ecological effects of dichlorobenzene can be found in Appendix A.

Trichlorobenzenes

Health Effects - 1,2,4-Trichlorobenzenes, as are the other chlorinated benzenes, are metabolized to phenols by the liver microsomal enzyme systems.(60) Trichlorobenzene produces histological changes in the liver and kidney.(59) This compound has slight to moderate acute toxicity for various aquatic species.(13) Its bioconcentration factor has been estimated as 182.(13)

Regulatory and Industrial Recognition of Hazard - The ACGIH TLV for 1,2,4-trichlorobenzene is 5 ppm. Because of the insufficiency of available information EPA could not derive a water quality criterion using the guidelines in effect in 1980. Additional information and references on the health and environmental effects of this substance can be found in Appendix A.

Tetrachlorobenzene

Health Effects - Chronic exposure of rats and dogs to tetrachlorobenzene affects the liver and the hemopoietic system (19,56). Tetrachlorobenzene is not acutely toxic to mammals, since its oral LD_{50} in the rat is 1500 mg/kg.(56) It is reported to be acutely toxic in varying degrees to some fresh- and saltwater organisms, and chronically toxic to saltwater organisms.(19) The predominant mammalian disposition site for tetrachlorobenzene is in the lipid tissues (16) of the body, and its bioconcentration factor was estimated to be 1800.$^{(13)}$

Tetrachlorobenzene was designated by Congress as a priority pollutant under §307 of the Clean Water Act of 1977.

For the protection of human health from the toxic properties 1,2,4,5-tetrachlorobenzene ingested through water and contaminated aquatic organisms, the ambient water criterion is determined to be 38 ug/l.$^{(13)}$

Additional information on the health and ecological effects of benzene can be found in Appendix A.

Pentachlorobenzene$^{(56)}$

Health Effects - Pentachlorobenzene is reported to be carcinogenic in mice, although not in rats or dogs. It is also reported to have caused bone defects in the offspring of rats which were exposed to this compound during gestation.

Pentachlorobenzene is quite acutely toxic at low concentrations (ranging from 160 ug/l to 6,780 ug/l) to both salt- and freshwater organisms, including plants.

Pentachlorobenzene has an extremely high octanol/water partition coefficient of 154,000, indicating a dangerously high bioaccumulation potential.(14)

For the protection of human health from the toxic properties of pentachlorobenzene ingested through water and contaminated aquatic organisms, the ambient water criterion is determined to be 74 ug/l.(13)

Pentachlorobenzene is designated as a priority pollutant under §307 of the Clean Water Act.

Additonal information on the adverse health effects of pentachlorobenzene can be found in Appendix A.

Hexachlorobenzene

Health Effects - U.S. EPA's Carginogen Assessment Group (CAG) has evaluated hexachlorobenzene and has found sufficient evidence to indicate that it is carcinogenic. It is also fetotoxic to rats.(23) The distribution of hexachlorobenzene is apparently the same in the fetus and the adult, with the highest concentration accumulating in fatty tissue. (23) Its estimated bioconcentration factor is very high: 22,000.(13)

Chronic exposure of rats to hexachlorobenzene has caused histological changes in the liver and spleen (24), and in humans, causes porphyrinuria and other symptoms of porphyria cutanea tarda.(25,26)

For protection of human health from the potential carcinogenic effects of exposure to hexachlorobenzene through ingestion of contaminated water and contaminated aquatic organisms the ambient water quality criterion was set at 72 ug/l (10^{-6} incremental cancer risk).(13)

Hexachlorobenzene is designated as a priority pollutant under §307 of the Clean Water Act.

Additional information on the adverse health effects of hexachlorobenzene can be found in Appendix A.

Benzyl Chloride

Health Effects - Benzyl chloride has been identified as a carcinogen (18), and is also mutagenic(27).

The OSHA TWA for benzyl chloride is 1 ppm. DOT requires labeling as a corrosive. The Office of Water and Waste Management, EPA, has regulated benzyl chloride under Section 311 of the Clean Water Act. Preregulatory assessment has been completed by the Office of Air, Radiation and Noise under the Clean Air Act. The Office of Toxic Substances has requested additional testing under Section 4 of the Toxic Substances Control Act.

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Benzyl chloride is listed in Sax's *Dangerous Properties of Industrial Materials* as highly toxic via inhalation and moderately toxic via the oral route.

Additional information and specific references on the adverse effects of benzyl chloride can be found in Appendix A.

2,4,6-Trichlorophenol

Health Effects - NCI has concluded that this compound is carcinogenic in mole F344 rats (inducing lymphomes and leukemias), and in both sexes of B_6, C_3, F_1, mice, inducing hepatocellular carcinogens and abensomas.(61) Accordingly, 2,4,6-trichlorophenol has also been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of carcinogenicity. 2,4,6-Trichlorophenol is lethal to humans by ingestion of 60% of the oral LD_{50} dose in rats [500 mg/kg].(43) This chemical is reportedly mutagenic(62) and adversely affects cell metabolism.(63,64) 2,4,6-Trichlorophenol has been designated a priority pollutant under 307(a) of the FWPCA.

Ecological Effects(14) - Very small concentrations of 2,4,6-trichlorophenol are lethal to freshwater fish [LC_{50} = 175-426 ug/l]; it is also lethal to freshwater invertebrates at very low concentrations.

Regulatory Recognition of Hazard - 2,4,6-Trichlorophenol has been designated as a priority pollutant under Section 307(a) of the CWA. Based on carcinogenicity, EPA has recommended 1.2 ug/l as the ambient water quality criterion for the ingestion of fish and water (10^{-6} excess cancer risk).(14)

Industrial Recognition of Hazard - Sax, in *Dangerous Properties of Industrial Materials*(45), lists 2,4,6-trichlorophenol as moderately toxic via ingestion.

Additional information and specific references on the adverse effects of 2,4,6-trichlorophenol can be found in Appendix A.

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Response to comments column bottoms and aqueous stream from the production of chlorobenzenes (K085).

1. One commenter characterized the Agency's use of the terms "chlorobenzene" and "chlorinated benzene", and its occasional general references to chlorobenzenes with higher degree of chlorination as "polychlorinated benzenes" as "shoddy and ambiguous". The commenter went on to remark that these isomeric compounds differ in physical properties, production, waste management, health and environmental effects. The Agency deems the terms "chlorobenzene(s)" and "chlorinated benzene(s)" to be acceptable, widely used synonymous chemical terms. However, in order to leave no room for ambiguity as to the chemical nature of the chlorinated benzenes which are of concern in these wastes, and in order to facilitate a comparison of their relevant properties, a figure illustrating their chemical structure and a table delineating their physical properties have been added to the Background Document.

2. One commenter disagreed with the listing of the separated aqueous stream from the reactor product washing step as hazardous. The commenter disputed the Agency's determination that phenols and chlorinated phenols will be found in this waste stream, stating that the reported occurence of these compounds in the untreated wastewater is atypical.

The commenter went on to state that the aqueous waste, in any case, contains pollutants at such low concentrations (i.e., 3-135 ppm, averaging 56 ppm) that the waste should be of no regulatory concern under RCRA.

The Agency disagrees with these comments. Phenol and chlorinated phenols are likely to be found in this waste in some concentration as stated in the background document, because chlorinated benzenes are known to form these compounds as a result of hydrolysis under alkaline conditions and elevated temperatures, conditions present during chlorobenzene manufacture.(58) The presence of these compounds in the sampled wastewater stream confirms this process assumption.

However, on further consideration, we have decided that certain of these compounds are not present in the waste in concentrations sufficient to warrant their inclusion as toxic constituents of concern. Phenol, 2-chlorophenol, and 2,4-dichlorophenol are in this category. Not only are the reported sampled concentrations already low, but they may be greater than concentrations normally present from processes involving only chlorobenzene manufacture, since the sampled waste may have included wastewater from chlorophenol manufacture.

We will continue to list the carcinogen 2,4,6-trichlorophenol as a constituent of concern. Since the reported concentration is many orders of magnitude above the recently promulgated human health Ambient Water

Quality Criterion for this compound (45 FR 79329 November 7, 1980), we believe the value to indicate a potential for hazard if the waste is mismanaged. We also believe that benzene and chlorinated benzenes may typically be present in substantial concentrations, namely their limits of solubility, and so will continue to list the waste for these constituents as well.

The commenter further argued that these constituents are amenable to biological treatment, and so should not be listed. The unstated thought is that although sludges resulting from wastewater treatment are hazardous (see §261.3), they may not contain appreciable concentrations of the constituents of concern if biological treatment is successful.

There are a number of answers to this comment. The Agency, in its July 16 Background Document invited commenters to show that their wastewater treatment sludges are not hazardous. No data on this waste were submitted by any commenter. Furthermore, the delisting mechanism remains available to any facility wishing to demonstrate that wastewater treatment sludges resulting from treatment of wastewater from chlorobenzene manufacture is not hazardous. Equally important, not all plants utilize biological treatment, so that the hazardous constituents could be present in some wastewater treatment sludges in much higher concentration than in others.

Even where biological treatment is used, the Agency has no assurance that the treatment is always successful in removing hazardous constituents from the sludge, since organisms must be specially adapted to degrade these toxic constituents. We thus do not believe the comment to be sufficiently persuasive to warrant deleting this waste listing.

3. The same commenter also mentioned in passing that it generates an aqueous waste stream from a continuous chlorobenzene manufacturing process, even though the background document indicated that this waste stream is generated only from batch processes.

   Available information continues to indicate that in most cases, there will be no wastewater stream generated from the continuous production of chlorobenzenes. In response to the comment, however, we are revising the listing description to include wastewater streams which arise from continuous processes. Since raw materials are the same and reaction processes are similar for both processes, we expect any wastewater to be similar in composition. The constituents and their concentrations shown in reference 29, an analysis of wastewater from a continuous process, is comparable to that predicted for batch processes, confirming our assumption.

4. One commenter criticized the Agency's characterization regarding the persistences, mobilities and toxicities of several chlorophenols. The commenter recommends that the Agency reassess the hazard of the aqueous process stream, since, in its view, phenols and chlorinated phenols are not hazardous constituents. Several of the comments raised are identical to those raised by the same manufacturer with respect to solid waste K043 (2,6-dichlorophenol waste from the production of 2,4-D). The Agency's reply to these comments were published on November 15, 1980 (Response to Comments, page 635 of the BD dated November 19, 1980). There is no need to repeat them here.

Based on the foregoing discussion, the Agency will continue to list wastes K085 (distillation or fractionating column bottoms from production of chlorobenzenes) and K105 (separated aqueous stream from the reactor product washing step in the batch production of chlorobenzenes) as hazardous.

SJ-39-14
January 1981

LISTING BACKGROUND DOCUMENT

K086: SOLVENT WASHES AND SLUDGES, CAUSTIC WASHES AND SLUDGES AND WATER WASHES AND SLUDGES FROM THE CLEANING OF TUBS AND EQUIPMENT USED IN THE FORMULATION OF INK FROM PIGMENTS, DRIERS, SOAPS AND STABILIZERS CONTAINING CHROMIUM AND LEAD LEAD (T).

I. SUMMARY OF BASIS FOR LISTING*

Tubs and equipment used in ink formulation are washed by solvents, caustics and/or water. The Administrator has determined that the spent washes and wash sludges generated after ink formulation in which pigments, driers, soaps and stabilizers containing hexavalent chromium and lead are used may pose a present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. The washes and sludges typically contain significant concentrations of lead and hexavalent chromium. Lead is highly toxic to a variety of species and is reportedly carcinogenic in laboratory animals. Hexavalent chromium is also toxic; in addition, EPA's Cancer Assessment Group has found that CR^{+6} exhibits substantial evidence of carcinogenicity.

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*The Agency is investigating the potential hazards of organic constituents of printing inks. We are, for instance, investigating the possible conversion by heat, light or reducing agents present in waste streams or the environment, of pigments derived from 3,3'-dichlorobenzidine to the parent (carcinogenic) amine. We are also concerned about wastes from the manufacture of jet printing inks containing direct dyes derived from benzidine, *o*-dianisidine and *o*-tolidine: such dyes could similarly be converted to the carcinogenic parent amine.

Organic solvents likely to be used in these washes are covered under listings F003, F004, and F005, §261.31, hazardous waste from nonspecific sources (45 FR 74890, November 12, 1980).

2. Present management practices may be inadequate to prevent the migration of hexavalent chromium and lead from a disposal site. Disposal practices subject to RCRA include landfilling, impoundment and removal by contract haulers. Such practices, if uncontrolled, can result in contamination of ground and surface waters by lead and hexavalent chromium.

II. INDUSTRY DESCRIPTION AND MANUFACTURING PROCESS(1)

An EPA survey of the ink formulating industry indicates that there are approximately 460 ink manufacturers in the United States (excluding captive ink producers that manufacture ink in a printing plant solely for use in that plant). The distribution of ink manufacturing plants by state is given in Table 1. In 1972, total ink production was greater than one billion pounds.

The variety of inks used today is broad, ranging from ordinary writing inks to specialized magnetic inks. Inks manufactured for the printing industry, which utilizes a major portion of ink production, fall into four major categories: letterpress inks, lithographic inks, flexographic inks, and gravure inks.

Letterpress inks are viscous, tacky pastes using vehicles that are oil and varnish-based. They generally contain resins and dry by the oxidation of the vehicle.

Lithographic or off-set inks are viscous inks with a varnish-based vehicle, similar to the letterpress varnishes. The pigment content is higher in lithographic inks than letterpress ink because the ink is applied in thinner films.

Table 1 (1)

DISTRIBUTION OF INK MANUFACTURING PLANTS BY STATE

State	Number of Plants	Percent of Plants
California	47	10.2
Illinois	46	10.0
New Jersey	39	8.5
New York	34	7.4
Ohio	28	6.1
Pennsylvania	24	5.2
Texas	22	4.8
Massachusetts	21	4.6
Georgia	20	4.3
Missouri	16	3.5
Florida	14	3.0
Wisconsin	14	3.0
Michigan	13	2.8
Tennessee	13	2.8
North Carolina	10	2.2
Louisiana	9	2.0
Maryland	9	2.0
Minnesota	9	2.0
Virginia	9	2.0
Indiana	7	1.5
Oregon	7	1.5
All Others	49	10.7

Flexographic inks are liquid inks which dry by evaporation, absorption into the substrate, and decomposition. There are two main types of flexographic inks: water and solvent. Water inks are used on absorbent paper and the solvent inks are used on nonabsorbent surfaces.

Gravure inks are liquid inks which dry by solvent evaporation. The inks have a variety of uses ranging from printing publications to food package printing.

Inks are either water, oil or solvent-based. The "average" plant produces approximately 60 percent oil base ink, 25 percent solvent base ink and 5 percent water base ink.

In the manufacture of inks, the major ingredients (vehicles, pigments and driers) are mixed thoroughly to form an even dispersion of pigments within the vehicle. The mixing is accomplished with the use of high-speed mixers, ball mills, three-roll mills, sand mills, shot mills, and/or colloid mills.

Most inks are made in a batch process in tubs ranging in sizes from 19 liters (five gallons) to over 3,750 liters (1,000 gallons). The number of steps needed to complete the manufacture of the ink depends upon the dispersion characteristics of the ingredients. Most inks can be completely manufactured in one or two steps since many of the pigments used can be obtained predispersed in a paste or wetted form.

III. GENERATION AND MANAGEMENT OF HAZARDOUS WASTE(1)

Ink is manufactured by blending raw materials; chemical reactions generally do not occur and no by-products are formed. When required, production tubs and manufacturing equipment are washed clean of residue from the formulation process. The spent cleaning solutions become contaminated with tank residue composed of the residual raw materials.

Four broad types of raw materials are used in ink manufacture:

- Pigments and dyes, flushes and dispersions
- Chemical specialties (including driers, plasticizers, soaps and stabilizers)
- Resins
- Solvents

Inorganic pigments are the primary source of (hexavalent) chromium and lead in ink industry wastewaters; chemical specialties are also reported to contain lead. Survey data obtained by EPA show that the ink formulation industry relies on inorganic pigments for about 40% of the total production. The two most widely used lead and chromium-containing pigments are chrome yellow and molybdate orange, although many other pigments are sources of lead and chromium in the waste. Chrome yellow is a compound consisting of lead, hexavalent chromium and oxygen; molybdate organge also contains lead and hexavalent chromium as well as molybdenum.

Particular chemical specialties are another significant source of lead and chromium in these wastes. For example, driers containing lead are used by approximately 30% of the industry.* Stabilizers (some containing lead and phenol), metallic soaps, and flatting agents containing lead are also in use and are expected to contribute significant concentrations of lead to process wastes.**

Process wastewater from ink manufacturing plants results primarily from the rinsing of mixing tubs, roller mills, and other equipment. Some additional wastewater may come from floor and spill cleaning, laboratory and plant sinks, boiler and cooling water blowdown, air pollution control devices using water, and cleanout of raw material supply tank cars or trucks.

The ink industry commonly uses three methods of ink tub cleaning: (1) solvent-wash; (2) caustic-wash; and (3) water-wash.

(1) Solvent-Wash Wastes

Solvent-wash is used exclusively to clean tubs used for formulating solvent-based and oil-based ink. The dirty solvent generally is handled in one of three ways:

1. used in the next compatible batch of ink as part of the vehicle;

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* Examples are Shephard-lead tallates, lead linoleates, Hexogan, Aduasol and Catalox.(1)

**Industry survey data indicate that approximately 70% of the manufacturers use chromium-containing raw materials, and 55% use lead-containing raw materials. Thus, use of materials containing these pollutants is widespread in the industry.

2. collected and redistilled, either by the plant or by an outside contractor for subsequent resale or reuse; or
3. reused with or without settling to clean tubs and equipment until spent, and then drummed for disposal. If sludge is settled out it is also drummed. These spent solutions and sludges are usually disposed of by contract hauling.

(2) Wash-Water Wastes

Water-washing techniques are used in both the solvent-base and water-base segments of the ink industry. For solvent-base operations, water-washing usually follows caustic washing of solvent-base tanks. For water-base operations, water washes often constitute the only tub cleaning operation, although water-base ink tubs may be cleaned periodically with caustic.

Wastewater generated by rinsing tubs or equipment used for manufacturing water-base ink is usually handled in one of four ways:

1. reused in the next compatible batch of water-base ink as part of the vehicle;

2. reused either with or without treatment to clean tubs and equipment until spent and disposed. If sludge is settled out it is disposed by contract hauling;

3. discharged with or without treatment as wastewater; or

4. disposed of immediately by contract hauling.

The water rinse following a caustic-wash is rarely reused in a subsequent batch of ink. The most common methods for disposal of this rinse are:

1. recycling it back into the caustic as make-up water;
2. drumming it for contract hauling;
3. discharging it as wastewater, with or without pretreatment. Combination with other wastewater prior to treatment or disposal is sometimes practiced. Discharge of this wastewater is currently prohibited by some states and municipalities and may be prohibited in other areas in the future.

(3) Caustic-Wash Wastes

Caustic wash techniques are used to clean both solvent-base and water-base ink manufacturing tanks. Plants using caustic rinse or washing systems usually rinse the caustic residue with water, although a few plants allow the caustic solution to evaporate in the tubs. There are several types of caustic systems commonly used by the ink industry. For periodic cleaning of fixed tubs two methods are popular:

1. maintaining the caustic in a holding tank (usually heated) and pumping through fixed piping or flexible hose to the tub to be cleaned. After cleaning, the caustic is returned to the holding tank; and
2. preparing the caustic solution in the tub to be cleaned, and soaking the tub until clean. The caustic solution is either transferred to the next tub to be cleaned, stored in drums or a tank for subsequent use, or is discarded.

For cleaning small portable tubs, three common methods are used by the ink industry:

1. pumping caustic from a holding tank (usually heated) to nozzles in a fixed or portable hood which is placed over the tub to be cleaned. The caustic drains to a floor drain or sump and is pumped back to the tank, or is pumped back directly from the tub;
2. maintaining an open top caustic holding tank. Small tubs are put into "strainers" and dipped into these tanks until clean; and

3. placing the tubs in a "dishwasher-like" device (which circulates hot caustic), and a subsequent water rinse. These devices can handle tubs up to about 1900 liters (500 gal).

Most plants using caustic, recycle the caustic solution until it loses some of its cleaning ability. The spent caustic is then disposed of either by contract hauling or as a wastewater, with or without neutralization or other treatment.

The most common methods of wastewater disposal are discharge to a sewer, contract hauling, evaporation, and landfill or impoundment. Most contract haulers discharge the sludge to a landfill, although a few incinerate or reclaim it.(1)

Although precise figures on the amount of waste covered by this listing are not available, the quantity is expected to be significant, and, furthermore, is expected to increase in the future. Final regulations issued by EPA's Effluent Guidelines Division impose zero discharge requirements for certain pollutants on all ink manufacturers in the solvent wash category of the industry except existing pre-treaters; proposed regulations would impose zero discharge requirements on existing pre-treaters in the Solvent Wash category and all others in the Caustic and/or Water Wash category. Implemementation of these regulations will increase the amount of hazardous waste requiring disposal in accordance with the RCRA Subtitle C regulations.

V. DISCUSSION OF BASIS FOR LISTING

A. HAZARDS POSED BY THE WASTE

Solvent washes and sludges, caustic washes and sludges and water washes and sludges from cleaning equipment used in the formulation of ink from raw materials containing lead and hexavalent chromium are listed as hazardous because they typically contain significant concentrations of lead and (presumably hexavalent) chromium.*

Lead is poisonous in all forms. It is one of the most hazardous of the toxic metals because it accumulates in many organisms and its deleterious effects are numerous and severe. Epidemiology studies implicate occupational exposure to hexavalent chromium in the induction of lung tumors. Impairment of pulmonary function is also reported to result from chronic exposure to hexavalent chromium. (For further information on Health and Ecological Effects of chromium and lead, see Section B (Health and Ecological Effects) in this background document, and Appendix A.

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* Other toxic metals and various toxic organics are also known to be present in some of the wash wastes, but sufficient data are not yet available to list the wastes for those contaminants. It also should be noted that the tub-cleaning wastes can exhibit hazardous characteristics other than toxicity; the Agency has information which indicates that the listed wastes can be ignitable or corrosive (3,4,5,6). In addition, a number of spent solvents are listed as hazardous in §261.31 of the hazardous waste regulations published on November 12, 1980 (45 FR 74890), and if these solvents are used in ink formulation and are disposed of, they are considered hazardous wastes under the earlier listing as well as the present listing. Listed solvents presently in use by the ink formulation industry include: toluene, 1,1,1-trichloroethane, ethyl benzene methylene chloride and trichloroethylene. Delisting petitions by ink formulators using these solvents must address not only the presence of the spent solvent itself in the waste, but the presence of lead and hexavalent chromium as well.

The following data substantiates the presence of significant concentrations of lead and chromium in the wash wastes:

- EPA has determined that the average concentrations of lead and chromium per day in ink industry caustic wash and water-wash wastewaters are 151 mg/l and 35 mg/l, respectively. Concentrations as high as 900 mg/l of lead and 200 mg/l of chromium were reported.(1)*

- A summary of industrial waste composition data taken from the manifests required by the State of California for transportation of hazardous wastes lists the following wastes from the manufacture of printing ink as hazardous:(2)

    1. Ink wastewater which contained 1000 ppm of lead.
    2. Equipment cleaning washwater which contained 10,000-20,000 ppm of lead chromate.

- "Special Waste Disposal Applications" were submitted to the State of Illinois for the following wastes from ink manufactures:(3)

    1. Solvent waste containing 120 ppm of chromium and 770 ppm of lead.
    2. Solvent waste containing 291 ppm of lead.

- A "Hazardous Waste Disposal Request" was submitted to the Missouri Department of Natural Resources for disposal of printing ink sludge (wash waste) containing 260 ppm of chromium and 1,340 ppm of lead.(4)

- The "Industrial Waste Surveys" file of the State of New Jersey contained a description of ink manufacturing wash water with 260 ppm of lead (7).

Clearly the concentrations of lead and chromium in the wastes may be very substantial.

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*These figures may be conservative in light of the higher concentrations contained in state manifests, given below.

The presence of such high concentrations of toxic metals in a waste in and of itself raises regulatory concerns. Lead and hexavalent chromium have proven capable of migration, mobility and persistence in many waste management settings(28), raising the concern that, if these wastes are improperly managed, the lead and hexavalent chromium may be released from the waste in harmful concentrations and adversely effect human health and the environment. Because lead and chromium do not degrade with the passage of time, they will provide a potential source of long-term contamination if they are permitted to escape from the disposal site.

Current disposal methods do not appear adequate to prevent migration of these toxic metals from the waste into the environment. Toxic metal-bearing liquid wastes placed in an impoundment can release those hazardous constituents to the surrounding area if seepage and overflow are not controlled, or measures are not taken to prevent total washout. Without regulation, proper containment of the impounded wash wastes cannot be assured.

Clearly, if measures to retard migration of liquids from impoundments and landfills are not employed, ground and surface waters could easily become contaminated. Improper landfilling of sludges settled from the liquid wastes could also result in release of the hazardous constituents. The heavy metal compounds might already be solubilized or may solubilize as a result of disposal conditions (co-disposal with acids, alkalis or decomposing organic matter, for instance) and could then migrate from the disposal site to ground and surface waters. As a result, ground and surface drinking water supplies may become contaminated, and wildlife and various aquatic species could be threatened by exposure to the toxic metals lead and hexavalent chromium.

Unregulated contract hauling of wastes by private disposal services, scavengers or purveyors in tank trucks -- a waste management method frequently used for these wastes -- creates additional hazards. There have been innumerable damage incidents involving unregulated contract hauling, resulting in substantial environmental harm. (Some examples are collected in Reference 28.) Thirty-one percent of the ink plants surveyed by EPA did not know what the contract hauler does with their waste.(1) There is obvious potential for abuse in this system since there is no way to determine whether these wastes are properly managed during transportation, treatment or disposal; irresponsible handling at any point could ultimately endanger human health and the environment. Therefore, it is essential that wastes of this nature be subject to regulation from "cradle to grave".

B. Health and Ecological Effects

1. Lead

Health Effects

Lead is poisonous in all forms. It is one of the most hazardous of the toxic metals because it bioaccumulates in many species, and its deleterious effects are numerous and severe. Lead may enter the human system through inhalation, ingestion or skin contact. The hematopoietic system is the most sensitive target organ for lead in humans, although subtle neurobehavioral effects are suspected in children at similar levels of exposure.(8)

Lead exposure has been reported to decrease reproductive ability in men(9) and women.(10) It has also been shown to cause disturbances of blood chemistry,(11) neurological disorders,(12,13), kidney damage(14) and adverse cardiovascular effects.(15) Lead has been shown to be teratogenic in animals.(16) Although certain inorganic lead compounds are carcinogenic to some species of experimental animals, a clear association between lead exposure and cancer development has not been shown in human populations.

Additional information and specific references on adverse effects of lead can be found in Appendix A.

Ecological Effects

In the aquatic environment, lead has been reported to be acutely toxic to invertebrates at concentrations as low as 450 ug/l and chronically toxic at less than 100 ug/l.(17) The comparable figures for vertebrates are 900 ug/l for acute toxicity(18) and 7.6 ug/l for chronic toxicity.(19) Lead is bioconcentrated by all species tested - both marine and freshwater - including fish, invertebrates and algae. The mussel, *Mytilus edulis*, concentrated lead 2,568 times that found in ambient water. Two species of algae concentrated lead 900-1000 fold. Algae reportedly can concentrate lead in their tissues to levels as much as 31,000 times ambient water concentrations.(20) Lead does not degrade with the passage of time and may be expected to persist indefinitely in the environment in some form.

Regulatory Recognition of Hazard

As of February 1979, the U.S. Occupational Safety and Health Administration has set the permissible occupational exposure limit for lead and inorganic lead compounds at 0.05 mg/m^3 of air as an 8-hour time-weighted average. The U.S. EPA (1979) has also established an ambient airborne lead standard of 1.5 ug/m^3.

The U.S. EPA's Office of Water Regulations and Standards has recommended an ambient water quality criterion for lead to protect freshwater aquatic life of 0.75, 3.8, and 20 micrograms lead per liter (ug/l) corresponding to a water hardness of 50, 100, and 200 mg/l calcium and carbonate. The ambient water quality criterion for lead to protect human health is recommended to be identical to the existing drinking water standard of 50 ug/l.(21)

In addition, final or proposed regulations of the States of California, Maine, Massachusettes, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define lead containing compounds as hazardous wastes or components thereof.(22)

Industrial Recognition of Hazard

Lead is rated as highly toxic through ingestion, inhalation and skin absorption routes in Sax, *Dangerous Properties of Industrial Materials*.

Chromium

Health Effects

Hexavalent chromium is an animal carcinogen and there is evidence that it may be a human carcinogen as well.(23) EPA's Carcinogen Assessment Group has listed it as such. Mutagenic effects in bacteria have also been described. Cytogenetic effects in workers using hexavalent chromium compounds have been reported.(24)

Teratogenic effects of chromium have been reported in a single study and have not been confirmed.

Impairment of pulmonary function has been described in chrome electroplating workers subject to chronic chromium exposure.(25)

Additional information and specific references on the adverse effects of chromium can be found in Appendix A.

Ecological Effects

Hexavalent chromium, at low concentrations, is toxic to many aquatic species. For the most sensitive aquatic species, *Daphnia magna*, a final chronic no-effect level of less than 10 ug/l has been derived by the U.S. EPA.

Regulatory Recognition of Hazard

The U.S. EPA's Office of Water Regulations and Standard has recommended an ambient water quality criterion for hexavalent chromium to protect freshwater aquatic life of 0.29 ug/l as a 24-hour average. For protection of saltwater aquatic life, the criterion for hexavalent chromium is 18 ug/l. The ambient water quality criterion for hexavalent chromium to protect human health is recommended to be identical to the existing drinking water standard which is 50 ug/l.(27)

The OSHA time-weighted average exposure criterion for chromium (carcinogenic compounds) is 1 ug/m^3; for the "non-carcinogenic" classification of chromium compounds the criterion is 25 ug/^{3} TWA.

For the protection of aquatic species, proposed water criteria for both trivalent and hexavalent chromium in freshwater and marine environments have been prepared in accordance with the Guidelines for Deriving Water Quality Criteria.(27)

Industrial Recognition of Hazard

Sax, *Dangerous Properties of Industrial Materials*, 4th Ed. 1975, rates chromium as having a high pulmonary toxicity.

References

K086: INK FORMULATION

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Response to Comments: Ink Formulation Waste Streams [Proposed Listing, December 18, 1978 (43 FR 58959)]

1. One commenter stated that the proposed listing is too broad and that all wash wastes should not be considered hazardous.

The listing of the above waste has been clarified. After reviewing available information, the Agency has narrowed the listing to cover wastes from the cleaning of equipment used to formulate ink from raw materials containing chromium and lead. Data show that raw materials containing chromium and lead are widely used in the industry, and the wash wastes generated when these raw materials are used are likely to exhibit substantial concentrations of these toxic metals. The Agency concluded that these wash wastes present a potential hazard to human health and the environment because improper disposal may result in the contamination of ground and surface waters used as drinking water sources (see the background document for a more detailed discussion).

2. One commenter stated that wash wastes should not be listed as corrosive since the corrosive waste streams can be neutralized.

The fact that the wastes can be neutralized does not mean that they are not hazardous when generated. In order to make sure that corrosive wastes are managed properly, corrosivity must be determined before treatment by neutralization or any other means (see §261.3(b)(3).

For the final listing, the Agency has decided not to characterize the wash wastes as corrosive because adequate data are not available to indicate that the wastes are typically corrosive as defined in §261.22. In addition, the Agency believes that the corrosivity of the wastes can easily be determined by the generator. Such a determination is required for all wastes not included in this listing, and for all wastes addressed by individual petitions for delisting. (See §§ 262.11, 260.22.)

3. The commenter stated that classification of all wash wastes as hazardous because some might contain toxic organic substances is arbitrary.

The Agency has narrowed its proposed listing, although the claims of the commenter are not particularly persuasive. The revised listing does not at this time address toxic organic substances in the waste. As additional data becomes available, the Agency may include such substances as toxic constituents of concern in these wastes. The Agency for instance, concerned with the use of phthalates used as plasticizers in ink formulation, and use of phenols in chemical specialties. Information is solicited as to concentrations of these materials in ink formulation wastes, and potential mass loadings of these pollutants.

The Agency is particularly concerned over any potential environmental degradation by heat, light, or chemical reducing agents of the diarylide yellow pigments to the parent amine, 3,3'dichlorobenzidine. Certain solvents used in ink formulation are listed as hazardous wastes under F002, F003, F004, and F005 (45 FR 33123, May 19, 1980).

CON-12-02
January 1981

LISTING BACKGROUND DOCUMENT

K087: Decanter Tank Tar sludge from coking operations* (T)

I. Summary of Basis for Listing

The spray cooling of coke oven gases during the by-product recovery process results in the generation of a decanter tank tar-sludge. The Administrator has determined that decanter tank tar-sludge may pose a present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1) The tank tar-sludge contains significant concentrations of phenol and naphthalene. Phenol and naphthalene are toxic to humans and aquatic life.

2) Phenol has leached in significant concentration from a waste sample tested in a distilled water extraction procedure. Although no leachate data is currently available for naphthalene, the Agency believes that, due to its presence in the tar in high concentrations and due to its relative solubility, naphthalene also may leach from the waste in harmful concentrations if the waste is improperly managed.

3) These tar-sludges are often land disposed in on-site landfills or dumped in the open. These methods may be inadequate to impede leachate migration and resulting groundwater contamination.

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*The listing description has been amended from that originally proposed on December 18, 1978 (43 FR 58959) which included two waste listings [i.e., Coking: Decanter tank tar and Coking: Decanter tank pitch/sludge]

Additional information substantiating the hazards associated with polyncuelar aromatic hydrocarbon constituents in this waste will be evaluated in an expanded listing background document for an integrated by-product coke-making process.

II. Waste Generation, Composition and Management

Coke, the residue from the destructive distillation of coal, serves as both a fuel and as a reducing agent in the making of iron and steel. Some coke plants recover by-products given off or created during the coke production process, and the recovery of by-products generates a sludge which is the listed waste in this document. There are 66 by-product coke plants, which generate an estimated 72,300 tons/yr of decanter tank tar-sludge. During the recovery of chemicals in the by-product coke production process, tar separates by condensation from coke oven gas and drains to a decanter tank. Recoverable oil fractions are decanted off the top and the tar sludge settles to the bottom.

Approximately 97% of this tar-sludge is elemental carbon. The remaining 3% consists of condensed tar materials. These condensed tar materials contain the waste constituents of concern, namely phenolic compounds and naphthalene, which are formed as a result of the destructive distillation of coal.

Based on a published reference, the condensed tar component contains, by weight, 2.2% naphthalene and 0.1% phenolic compounds(2). With an estimated 2,169 tons/yr of condensed tar contained in the amount of tar-sludge generated annually (i.e., 3% of the 72,300 tons/yr of tar-sludge), approximately 47.7 tons of naphthalene and 2.2 tons of phenolic compounds will be contained in the waste generated each year(1,2).

Of the 66 coke plants generating decanter tank tar-sludge, 30 plants use the tar-sludge as a raw material in either the sintering process or open hearth furnace operation. The remaining 36 plants dispose of this waste in unsecure on-site landfills(1), or by dumping in the open(3).

III. Hazardous Properties of the Waste

Phenol and naphthalene are present in the tar component of this waste in significant concentrations: 0.1% by weight (1000 ppm) and 2.2% by weight (22,000 ppm), respectively(2). Phenol and naphthalene are toxic to humans and aquatic life. Thus, the Agency believes that the concentrations of these materials in the waste are quite significant, in light of the constituents' known health hazards. Further, these waste constituents appear capable of migrating in significant concentrations if mismanaged, and are likely to be mobile and persistent so that waste mismanagement could result in a substantial human health or environmental hazard.

Phenol's potential for migration from this waste in significant concentrations has been demonstrated empirically. Phenol leached in significant concentration (approximately 500 ppm) from a decanter tar-sludge waste sample subjected to distilled water extraction procedure.(3) In addition, phenol is extremely soluble, about 67,000 ppm @ 25°C(5), indicating high potential for migration. Phenol biodegrades at a moderate rate in surface water and soil but moves very readily (App. B). Even with a persistence of only a few day, the rapid spreading of phenol could cause widespread contamination of the eco-system and contamination of potable water supplies.

The migratory potential of phenol and its ability to move through soils is further confirmed by the fact that it has been detected migrating from Hooker Corporation's S Area, Hyde Park, and 102nd St. landfills in Niagara, New York (OSW Hazardous Waste Division, Hazardous Waste Incidents, Open File, 1978). The compound's persistence following migration is likewise shown by these incidents.

Although no comparable leachate data is currently available for naphthalene, the Agency believes that this constituent also may leach in harmful concentrations from the waste if not properly managed. The water solubility of naphthalene has been reported to range from 30 to 40 mg/1, depending on the salinity of the dissolving medium (7). Naphthalene has been identified in finished drinking water, lakes, and rivers, demonstrating its persistence and mobility (4). This information, naphthalene's solubility in water, and its presence in the tar in such high concentrations (22,000 ppm) make it likely that it will leach from the waste in potentially harmful concentrations if the waste is mismanaged, and will then be mobile and persistent, and so poses the potential for causing substantial hazard to human health and the environment.

Current practices of disposing of this waste in fact appear inadequate. Disposal of decanter tank tar-sludge in unsecured landfills or by dumping in the open makes it likely that the hazardous constituents in the waste will leach out and migrate into the environment, possibly reaching and contaminating drinking water sources. Siting of waste management facilities in areas with highly permeable soils could facilitate leachate migration. As demonstrated above, the waste constituents appear capable of migration, mobility and persistence. Thus, if disposal sites are improperly managed or designed (e.g., lack adequate leachate collection systems), waste constituents could leach into soils and contaminate groundwater.

Health and Ecological Effects

Phenol

Congress designated phenol a priority pollutant under §307(a) of the Clean Water Act.

Phenol is readily absorbed by all routes. It is rapidly distributed to mammalian tissues. This is illustrated by the fact that acutely toxic doses of phenol can produce symptoms within minutes of administration regardless of the route of entry. Repeated exposures to phenol at high concentrations have resulted in chronic liver damage in humans.(3) Chronic poisoning, following prolonged exposures to low concentrations of the vapor or mist, results in digestive disturbances (vomiting, difficulty in swallowing, excessive salivation, diarrhea), nervous disorders (headache, fainting, dizziness, mental disturbances), and skin eruptions(4).

Chronic poisoning may terminate fatally in some cases where there has been extensive damage to the kidneys or liver.

The Office of Water Regulations and Standards, U.S. EPA(6) has found that acute and chronic toxicity of phenol to freshwater aquatic life occur at concentrations as low as 10,200 and 2,560 ug/1, respectively, and would occur at lower concentrations in more sensitive species than those tested. The available data for phenol indicate that acute toxicity to saltwater aquatic life occurs at concentrations as low as 5,800 ug/1 and would occur a lower concentrations among species that are more sensitive than those tested. Based on available toxicity data, the ambient water quality criteria level for phenol to protect human health is 3.5 mg/1. The ambient water criteria level to control undesirable taste and odor qualities, the estimated level is 0.3 mg/1.

OSHA has set a TLV for phenol at 5 ppm. Phenol is listed in Sax's Dangerous Properties of Industrial Materials as highly toxic via an oral route.(4) Sax also describes phenol as a co-carcinogen and a demonstrated carcinogen via a dermal route in studies done with laboratory animals. Additional information and specific references on the adverse effects of phenol can be found in Appendix A.

Naphthalene

Naphthalene is designated as a priority pollutant under Section 307(a) of the CWA.

Systemic reaction to acute exposure to naphthalene includes nausea, headache, diaphoresis, hematuria, fever, anemia, liver damage, convulsions and coma. Industrial exposure to naphthalene appears to cause increased incidence of cataracts. Also, hemolytic anemia with associated jaundice and occasionally renal disease from precipitated hemoglobin has been described in newborn infants, children, and adults after exposure to naphthalene by ingestion, inhalation, or possibly by skin contact.

The Office of Water Regulations and Standards, U.S. EPA(7) has found that acute and chronic toxicity to freshwater aquatic life occur at concentrations as low as 2,300 and 620 ug/l, respectively, and would occur at lower concentrations among species that are more sensitive than those tested. The available data for naphthalene indicate that acute toxicity to saltwater aquatic life occurs at concentrations as low as 2,350 ug/l and would occur at lower concentrations among species that are more sensitive than those tested. Using the present guidelines, a satisfactory criterion for ambient water quality could not be derived at this time because of the insufficiency of data for naphthalene.

OSHA's standard for exposure to vapor for a time-weighted industrial exposure is 50 mg/m^3.

Sax lists naphthalene as moderately toxic via the oral route and warns that naphthalene is a demonstrated neoplastic substance via the subcutaneous route in experiments done on laboratory animals(4). Additional information and specific references on the adverse effects of naphthalene can be found in Appendix A.

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K087: Coking:Decanter Tank Car Sludge.

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Response to Comments: Coking - Decanter Tank Tar/Sludge.

One commenter stated that the Agency has misstated the scientific evidence for the waste constituents phenol and naphthalene with respect to attributing potential carcinogenicity to these two constituents.

The Agency agrees with the commenter and has revised the listing background document in a manner consistent with the toxicological analyses contained in Appendix A - Health and Environmental Effects Profiles of Subtitle C - Identification and Listing of Hazardous Waste, RCRA. However, the Agency still believes that these contaminants exhibit sufficient toxicity to be of regulatory concern. More specifically, prolonged exposure to low concentrations of phenol can result in digestive disturbances, nervous and skin disorders. Similar exposure to naphthalene can cause liver and renal disease.